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Experimental and theoretical studies of the binding interaction between copper(I) cation and the carbonyl group Substituent effect on the stability of (acetophenone)$_2$Cu$^+$ complex in the gas phase

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Abstract

The free energy changes (ΔG, copper cation basicity) for the reaction $L_2Cu^+ = Cu^+ + 2L$ were obtained in the gas phase for *m*- and *p*-substituted acetophenones based on the measurement of ligand-exchange equilibria using an FT-ICR spectrometer. A plot of the relative copper cation basicities (ΔCCB[L_2Cu^+]) against the ΔGBs (proton basicities) showed a limited linear relationship for *meta* substituents and *para* electron-withdrawing groups with a slope of 1.24. Negative deviations observed for strong π-donor substituents suggested that the resonance effect of these substituents is reduced in the Cu$^+$ complex compared to that in the protonated acetophenone. Based on the correlation analysis using the Yukawa–Tsuno equation, $\Delta G = \rho(\sigma^\circ + r\,\Delta\bar{\sigma}_R^+)$, the substituent effect on ΔCCB[L_2Cu^+] was characterized by a ρ value (kJ mol$^{-1}\bar{\sigma}^{-1}$ unit) of −56.2 and an r value of 0.60. The ρ value of −37.5 for monomeric complex (LCu$^+$) could be evaluated from a ρ value for L_2Cu^+ by using a correction coefficient of 1.5 given by the theoretical calculations. In comparison with the corresponding results for other Lewis cation basicity of the acetophenone system, it has been shown that the ρ value decreases in the order of H^+ (−48.5) > Me_3Si^+ (−46.0) > Me_3Ge^+ (−40.6) > Cu^+ (−37.5) > Li^+ (−34.7). The decrease in the ρ value indicates that the positive charges at the Lewis cation moiety of the adduct ion increases in this order. This is consistent with increasing ionic (ion–dipole interaction) nature of the bonding interaction between Lewis cations and the carbonyl oxygen atom. The r value that is a measure of the degree of charge-delocalization into the aromatic π-system decreases also in the same order.

Keywords: Copper(I) cation basicity; Ligand-transfer equilibrium; Acetophenones; Substitutent effect

1. Introduction

Metal ion complexes have been intensively studied in the condensed phase because the interactions between metal ions and organic ligands are important chemical and biological processes occurring in solution, such as ion solvation, molecular recognition, ion transport through membranes, and affinity of active compounds toward receptors [1–3]. An alternate approach is to study the thermochemistry of the complexes in the gas phase where solvent molecules and counter ions are absent. Under these conditions, the intrinsic bonding characteristics are most directly revealed. In addition, the differences in complexation energies between gas phase and solution elucidate the role of the solvent. However, the thermochemical data of the transition metal ion complexes are limited compared to alkali metal ions, particularly lithium ion. Among transition metal ions copper ion complexes have been studied relatively in detail and the thermochemical quantities such as copper cation basicity and/or affinity were determined for a variety of organic compounds by using different experimental techniques, such as equilibrium constant determination by pulsed high pressure mass spectrometry [4] and ion cyclotron resonance spectrometry [5], unimolecular dissociation [6], and energy-resolved collision-induced dissociation [7–10].

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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 $\Delta G_1 = -\text{RT}\ln K_1$ and $\text{CCB} = \Delta G_1$. In a similar manner, the gas phase copper cation affinity (CCA) is defined as the enthalpy change of the reaction (Eq. (1)), $\text{CCA} = \Delta H_1$. Jones and Staley have first provided the extensive experimental gas phase study of the bond energies of L_2Cu^+ complexes [5]. These data were based on the determination of ligand-exchange equilibria:

$$^1L_2Cu^+ + {}^2L = {}^1L^2LCu^+ + {}^1L \tag{2}$$

$$^1L^2LCu^+ + {}^2L = {}^2L_2Cu^+ + {}^1L \tag{3}$$

$$^1L_2Cu^+ + 2\,{}^1L = {}^2L_2Cu^+ + 2\,{}^1L \tag{4}$$

where ^1L and ^2L are two different ligands. Recently, Deng and Kebarle determined more strongly bonding complexes than the ligands used by Jones and Staley [4]. In these studies, the L_2Cu^+ complexes rather than LCu^+ were choosen owing to experimental convenience. Since the first two bond energies Cu^+–L and CuL^+–L are approximately equal and much higher than those observed with additional ligands [7–15], the special stability of L_2Cu^+ enables the measurements of the exchange equilibria. Although these results may provide somewhat restricted information, they are very valuable because they deal with the first two strongest bonding interactions.

The nature of the binding interactions between M^+ and organic ligands was often discussed from comparisons with basicity scales for other Lewis acids and a proton [4,5,16–19]. Jones and Staley found that there is a considerably fair linear relationship between $\Delta H(L_2Cu^+)$ and $\Delta H(LMn^+)$ for the oxygen bases with large deviations of R_2S, NH_3, and HCN [5]. Deng and Kebarle observed also similar deviations in plots of binding energies for L_2Cu^+ versus LLi^+ and L_2Ag^+ [4]. These deviations from the limited linear correlation for the oxygen bases were in part interpreted by the hard and soft acids and bases principle. In addition, the slopes of the correlation plots of the other reference acids versus Cu^+ were discussed in relation with the metal–ligand bond distance. However the actual bond energies are affected also by other important interactions such as electrostatic contributions due to ion–ligand dipole attractive forces. Furthermore, it is frequently found that there are family-dependent linear relationships between Lewis cation affinity (basicity) and proton affinity (basicity) with a difference slope for each family. A choice of a reference ligand series is obviously important to discuss the linear relationship between two systems and/or the deviations from their correlations. Indeed, a detailed comparison of lithium cation basicities with proton basicities showed that ethers, alcohols, and carbonyl compounds have the linear relationships for respective sub-families although the binding site of all these compounds is oxygen [17,18]. These results reveal that the deviations from the linear relationship result from the differences in many factors that contribute to the binding interaction of Lewis cations with organic bases. Accordingly, in order to understand the nature of the bond formed by Cu^+ it is necessary to separate quantitatively the overall 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, a particular interesting subset of ligands is aromatic compounds with a single basic site of which the electronic properties can be varied by the remote ring-substituent. Recently, we applied this approach to the study of the binding interaction of the lithium cation as well as other Lewis cation such as Me_3Si^+ and Me_3Ge^+ with neutral organic molecules [19–21]. The same approach will be applied to the interaction between copper cation and organic ligands. In this study, we therefore determined the copper cation basicity for *m*- and *p*-substituted acetophenones of which thermodynamic data such as gas phase basicities and Lewis cation basicities are available for comparison [19–22].

2. Experimental

2.1. 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 reactions (3) and (4) were similar to those used for the lithium cation basicity measurements described previously [19,23]. 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 [24]. 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 $(^1L_2Cu)^+$, $(^1L^2LCu)^+$, and $(^2L_2Cu)^+$ were measured based on the 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 of 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 ΔG at 343 K with an average uncertainty of $\pm 1\,\text{kJ mol}^{-1}$ in most of these cases. The occurrence of the ligand-transfer reaction was examined by an ion-eject experiment using the SWIFT technique [25].

2.2. Chemicals

Acetophenone derivatives used in this study were available from our previous studies [22]. 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 using an FT-ICR mass spectrometer.

2.3. Computational details

Theoretical calculations were carried out using the Gaussian 03 program suite [26]. 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 B3LYP/6-311+G(2d,2p) with B3LYP/6-311+G(3df) for Cu and MP2/6-311+G(2d,2p) levels of theory using the B3LYP/6-311G and B3LYP/6-31+G* optimized geometries. To obtain thermochemical quantities, the enthalpy and free energy corrections were applied. No corrections for the basis set superposition error (BSSE) were made [27], because the magnitude of BSSE was found to be small.

3. Results

3.1. 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 mass spectrometer. When two acetophenone derivatives ^1L and ^2L were present in the ICR cell, initial reactions forming $^1LCu^+$ and $^2LCu^+$ were followed by further addition of ligands to produce the dimeric adducts, $(^1L_2Cu)^+$, $(^1L^2LCu)^+$, and $(^2L_2Cu)^+$ within a second as shown Fig. 1(a). 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 (ΔG_4) for two ligands exchange reaction (4) is given by Eq. (5).

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

Fig. 1(b) shows a typical time profile for dimeric adduct ions of acetophenones with Cu^+. On the basis of ligand-exchange equilibria measurements involving 16 different acetophenones free energy changes ΔG_4 for the reaction (Eq. (4)) were obtained. The obtained ΔG_2, ΔG_3, and ΔG_4 values for respective equilibria are given in Table 1. From these results a ladder of the CCB[L_2Cu^+] was constructed as shown in Table 2. These relative scales were converted to absolute values for CCB by calibrating to the known value for MeCN, of which value was recently revised on the basis of threshold collision-induced dissociation measurements [8]. The ΔG 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 relative gas phase basicities (ΔGB[H^+]) toward a proton determined previously in our laboratory [22].

3.2. Theoretical calculations

3.2.1. Geometries of L_2Cu^+ and LCu^+ complexes, and CCBs and CCAs

The geometries of the neutral acetophenone and the corresponding monomeric and dimeric complexes with Cu^+ were optimized at several levels of theory. The selected geometrical parameters, CCAs, and CCBs are given in Table 2.

The optimized structures of (acetophenone)$_n$$Cu^+$ ($n = 1$ and 2) are illustrated in Fig. 2 along with values for selected bond distances and bond angles. The bond angle of CuO8C7 is 133–136° in the monomeric and dimeric complexes, while Chu et al. reported that Cu^+ aligns with the axis of the C=O bond (CuOC = 179.9°) in the (acetone)$_n$$Cu^+$ ($n = 1$ and 2) complexes on the basis of the B3LYP/6-31G* optimization [10]. However, the optimized structures of (acetone)$_2$$Cu^+$ obtained at the levels

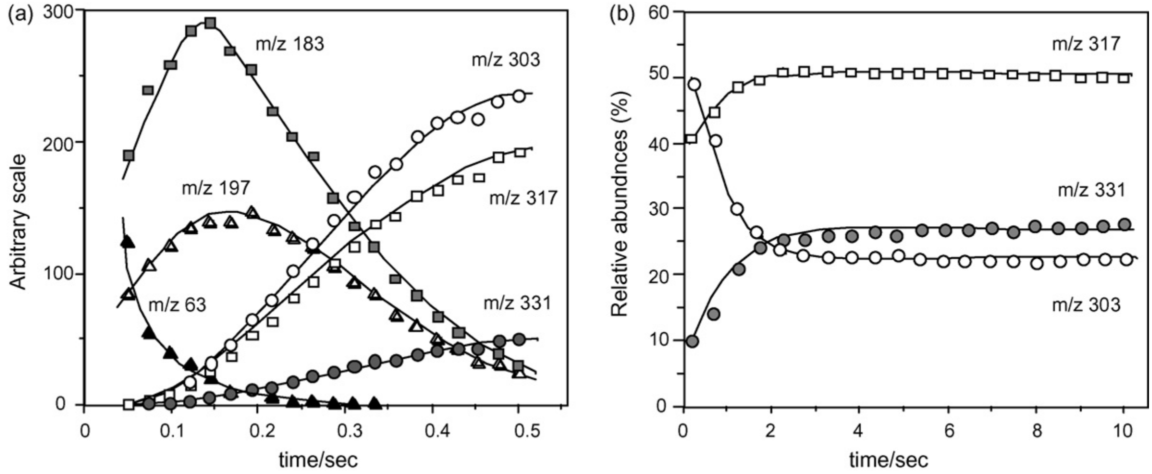


Fig. 1. Time profile of copper complexes formed from a binary mixture of *m*-methylacetophenone and acetophenone (*m*-MeC_6H_4COMe: 2.0×10^{-5} Pa, C_6H_5COMe: 7.6×10^{-5} Pa). (Closed triangles) *m*/*z* 63: Cu^+, (closed squares) *m*/*z* 183: $(C_6H_5COMe)Cu^+$, (open triangles) *m*/*z* 197: (*m*-$MeC_6H_4COMe)Cu^+$, (open circles) *m*/*z* 303: $(C_6H_5COMe)_2Cu^+$, (closed circles) *m*/*z* 317: $(C_6H_5COMe)Cu^+$(*m*-MeC_6H_4COMe), (squares) *m*/*z* 331: (*m*-$MeC_6H_4COMe)_2Cu^+$.

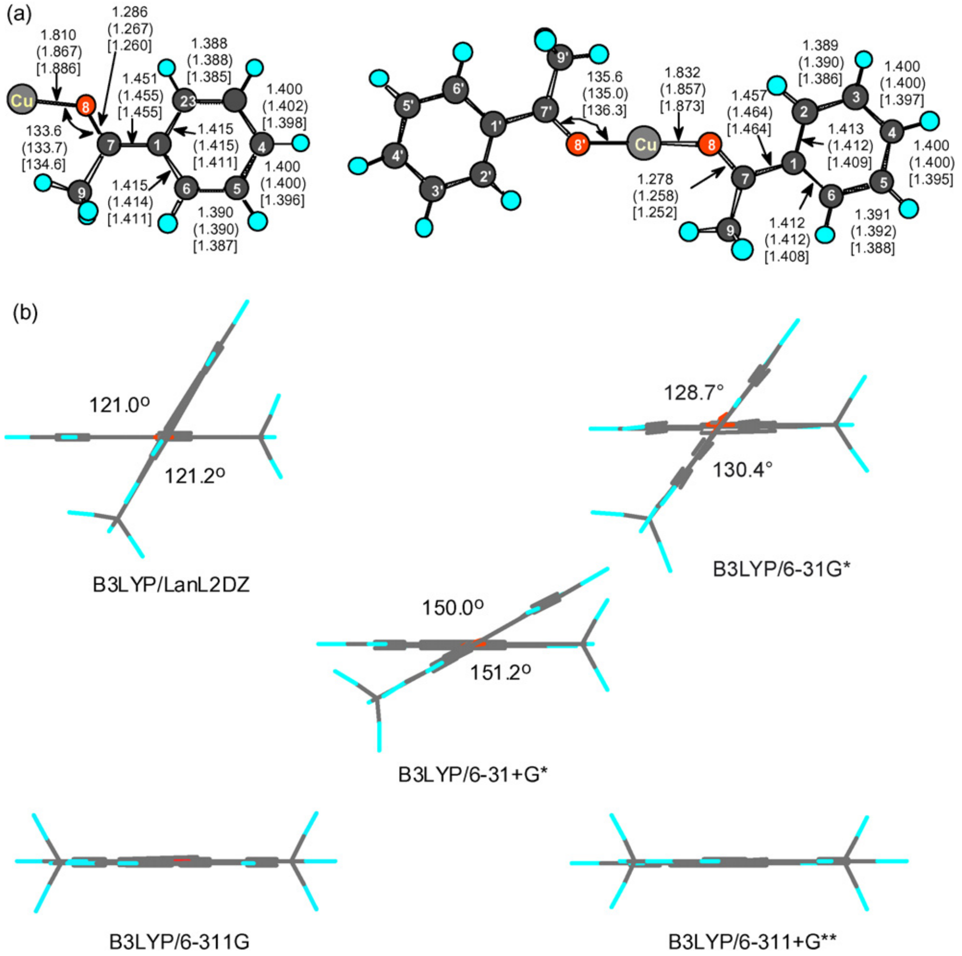


Fig. 2. (a) Optimized geometries of (acetophenone)Cu^+ and $(acetophenone)_2Cu^+$. Values are bond distances (Å) and bond angles (degree) calculated at B3LYP/6-311G, no parentheses, B3LYP/6-31+G* (round parentheses), and B3LYP/6-311+G** [square parentheses]. (b) The side views of $(acetophenone)_2Cu^+$ optimized at the indicated levels of theory. Values are dihedral angles (C2C1C1′C2′ and C8C7C7′C8′) in degree.

of theory, B3LYP/6-311G, B3LYP/6-31+G*, and B3LYP/6-311+G**, indicated the CuOC bond angles of 138.0°, 136.8°, and 138.2°, respectively, being consistent with the bond angles of the $(acetophenone)_nCu^+$ complexes ($n = 1$ and 2). These values of the bond angle of CuOC are intermediate between the corresponding angles in the protonated species, in which the covalent bond is formed between a base and a proton, and in the Li^+ complexes, suggesting the some covalent character in the Cu^+ interaction.

The two phenyl groups in the dimeric complex were found to lie in a plane as a larger basis set was used as shown in Fig. 2(b). The planar structures were also found at B3LYP/LanL2DZ and B3LYP/6-31+G* as a local minimum but they are only 0.08 and 0.13 kJ mol^{-1}, respectively, less stable than the twisted structure, suggesting that the potential surface is nearly flat with respect to the deviation from the planar structure. The bond distances also vary slightly with the basis set used for the calculations. In particular, the CuO8 distance in the dimeric complex increases from 1.800 Å (B3LYP/6-31G*) to 1.873 Å (B3LYP/6-311+G**) while the change in 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 the level of theory and basis sets, the calculated binding energies at the B3LYP/6-311+G(2d,2p) level of theory with an extended basis set of B3LYP/6-311+G(3df) for Cu are nearly identical regardless of optimized structures except for the B3LYP/6-31G* geometries. We therefore used the B3LYP/6-311G and B3LYP/6-31+G* optimized geometries for the energy calculations of a series of $(acetophenone)_nCu^+$ ($n = 1$ and 2) complexes because of convenient computing time although there is no experimental data to judge the best level of theory and basis set for the present system. The binding energies obtained at the MP2/6-311+G(2d,2p) also show a similar trend on the change of the geometries. However, while the B3LYP calculated CCB[L_2Cu^+] values of 381–385 kJ mol^{-1} for acetophenone is in good agreement with the experimental value (685.5 kJ mol^{-1}) within so-called chemical accuracy (8 kJ mol^{-1}) in absolute scale, the CCB and CCA values obtained at the MP2 calculations are consistently smaller than the corresponding values from the B3LYP calculations by 22 kJ mol^{-1}. Similar differences between B3LYP and MP2 calculations were observed for $(acetone)_nCu^+$ complexes [9].

Table 1
Free energy changes (ΔG) for ligand-exchange equilibira: ${}^1L_2Cu^+ + {}^2L = {}^1L^2LCu^+ + {}^1L$ (2), ${}^1L^2LCu^+ + {}^2L = {}^2L_2Cu^+ + {}^1L$ (3), and ${}^1L_2Cu^+ + 2{}^1L = {}^2L_2Cu^+ + 2{}^1L$ (4)

${}^1L$	${}^2L$	ΔG_2	ΔG_3	ΔG_4
p-MeO	MeCN	−9.8	2.9	−6.9
p-MeO	3,4-Me$_2$	−6.3	−2.6	−8.9
MeCN	3,4-Me$_2$	−5.6	4.0	−1.6
MeCN	*p*-MeS	−7.2	5.0	−2.2
MeCN	3,5-Me$_2$	−6.2	2.4	−3.8
3,4-Me$_2$	*p*-MeS	−2.6	1.2	−1.4
3,4-Me$_2$	3-Cl-4-MeO	−5.6	−1.1	−6.7
p-MeS	3,5-Me$_2$	−2.1	1.0	−1.1
3,5-Me$_2$	*p*-Me	−5.0	0.8	−4.2
3,5-Me$_2$	3-Cl-4-MeO	−3.9	0.3	−3.6
p-Me	3-Cl-4-MeO	−2.5	2.0	−0.5
p-Me	*m*-MeO	−5.1	−1.1	−6.2
3-Cl-4-MeO	*m*-Me	−5.5	−1.8	−7.3
m-MeO	*m*-Me	−2.6	1.9	−0.7
m-MeO	H	−6.9	−1.7	−8.6
m-Me	H	−6.1	−2.2	−8.3
H	*n*-Pr$_2$CO	−2.6	1.5	−1.1
H	*p*-COMe	−6.9	−2.4	−9.3
H	*p*-F	−8.1	−3.1	−11.2
n-Pr$_2$CO	*p*-F	−6.4	−2.6	−9.0
n-Pr$_2$CO	*p*-Cl	−7.7	−3.6	−11.3
p-COMe	*p*-Cl	−3.4	−0.1	−3.5
p-COMe	*p*-F	−3.4	0.4	−3.0
p-F	*p*-Cl	−3.3	1.5	−1.8
p-F	*m*-Cl	−4.1	−0.9	−5.0
p-Cl	*m*-F	−5.3	−1.3	−6.6
m-Cl	*m*-F	−3.3	0.3	−3.0
m-Cl	*m*-CF$_3$	−8.1	−4.1	−12.2
m-Cl	*p*-CF$_3$	−9.0	−5.6	−14.6
m-F	*m*-CF$_3$	−7.8	−1.5	−9.3
m-F	*p*-CF$_3$	−8.1	−4.4	−12.5

All values in kJ mol^{-1}. Ligands indicated are substituted acetophenones except for acetonitrile and dipropylketone.

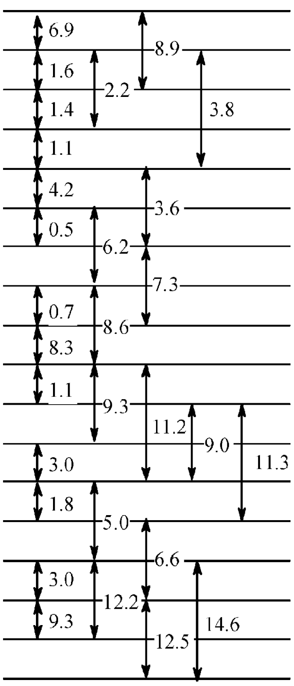
3.2.2. *Comparison of binding energies of Cu$^+$ between the first and second ligands*

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 [7–15]. Indeed, recent experimental data for H$_2$O, NH$_3$, (Me)$_2$O, MeCN, and acetone indicate that the second binding energy is identical to the first one [7–10]. This result was also consistent with theoretical calculations. However, it is found that, although there is a good linear relationship between the first binding energy and the sum of the first and second binding energies, a slope of the linear relationship is not 2.00 but 1.91 (Eq. (6)).

$$\Delta H[L_2Cu^+]_{exp} = 1.91\,\Delta H[LCu^+]_{exp} + 27.1 \quad (R^2 = 0.997) \tag{6}$$

The slope of 1.91 indicates that the binding energy for the second ligand is slightly reduced compared to that for the first ligand as the ligand is more basic. This suggests that the first binding energy cannot simply be predicted by dividing that for two ligands by a statistical factor of 2. If this relationship (Eq. (6)) is held for the present acetophenone system, it is possible to predict the free energy change for the first ligand, CCB[LCu$^+$], from the experimental CCB[L$_2$Cu$^+$] values. Since the ligands of which the first and second binding energies were determined experimentally are limited and considerably small in size compared to the acetophenone derivatives, it is necessary to examine whether the correlation given by Eq. (6) is also held for the present system. This is another aim for the present theoretical calculations because the copper cation basicities, CCB[LCu$^+$], for monomeric complex, (acetophenone)Cu$^+$, could not be determined in the present measurements based on the ligand-exchange equilibrium method. The calculated CCBs and CCAs for acetophenone given in Table 3 indicate that the binding energy with the first ligand is clearly larger than the second one regardless of the levels of theory used for calculations. Koizumi et al. reported that MP2 rather than B3LYP calculations for (acetone)$_n$Cu$^+$ (n = 1 and 2) complexes yield similar first and second binding energies, being consistent with the experimental results, and noted that 4s–3d σ hybridization is not as effectively described in DFT calculations as in MP2 theory [9]. The results given in Table 4 indeed show that the MP2 calculations gave relatively similar first and second binding energies compared to the DFT calculations; however, the second binding energies obtained by MP2 calculations are still smaller

Table 2
Measured free energy changes (ΔG_4) for ligand-exchange equilibira; ${}^1L_2Cu^+ + 2{}^2L = {}^2L_2Cu^+ + 2{}^1L$, copper cation basicities (CCB[L$_2$Cu$^+$]), and the corresponding gas phase basicities (ΔGB)

Acetophenones	Measured ΔG_4	CCB[L$_2$Cu$^+$] [a]	ΔCCB	ΔGB [b]
p-MeO		415.5	30.0	33.9
CH$_3$CN		408.8 [c]		
3,4-Me$_2$		407.1	21.6	21.3
p-MeS		406.0	20.5	27.2
3,5-Me$_2$		405.0	19.5	16.3
p-Me		400.8	15.3	16.7
3-Cl-4-MeO		400.6	15.3	25.6
m-MeO		394.4	8.9	11.3
m-Me		393.6	8.1	7.1
H		385.5	0.0	0.0
n-Pr$_2$CO		384.4		
p-COMe		376.2	-9.3	-7.1
p-F		374.3	-11.2	-2.5
p-Cl		372.8	-12.7	-2.5
m-Cl		369.3	-16.2	-13.8
m-F		366.2	-19.3	-15.5
m-CF$_3$		357.0	-28.5	-22.2
p-CF$_3$		354.2	-31.3	-24.3

All values in kJ mol^{-1}.
[a] Absolute scales of CCB[L$_2$Cu$^+$].
[b] Ref. [22].
[c] CCB of acetonitrile obtained from Ref. [8].

Table 3
Selected bond lengths and angles of (acetophenone)$_n$Cu$^+$ complex (n = 1 and 2), and calculated copper cation affinities (CCA) and basicities (CCB)

Basis set[a]	n	Bond distance (Å)			Bond angle (degree)		B3LYP[b,c] (kJ mol^{-1})		MP2[c,d] (kJ mol^{-1})	
		CuO7	C7O8	C1C7	CuOC	OCuO	CCA	CCB	CCA	CCB
6-31G*	1	1.764	1.271	1.445	124.0		234.7	201.7	211.3	178.2
6-311G	1	1.810	1.286	1.451	133.6		251.0	219.7	224.1	192.7
6-31+G*	1	1.867	1.267	1.455	133.7		251.0	220.1	225.1	194.5
6-311+G**	1	1.886	1.260	1.455	134.6		250.6	219.7	225.5	194.6
6-31G*	2	1.800	1.262	1.455	126.9	177.4	441.4	362.7	429.7	350.6
6-311G	2	1.832	1.278	1.457	135.6	180.0	456.9	381.2	435.7	359.7
6-31+G*	2	1.857	1.258	1.464	135.0	178.0	457.3	383.7	436.3	362.7
6-311+G**	2	1.873	1.252	1.464	136.3	180.0	456.9	384.5	338.9	362.8

[a] Basis sets used for the B3LYP optimization of geometries.

[b] B3LYP/6-311+G(2d,2p) level of theory with an extended basis set of B3LYP/6-311+G(3df) for Cu.

[c] Thermal corrections were applied using the frequency analysis at the indicated level of theory. No BSSE corrections.

[d] MP2/6-311+G(2d,2p).

than the first binding one. The differences between the first and second binding energies seem not to result from the method of calculations. This result may indicate that in the dicoordinated complex of acetophenone the repulsive interaction between two ligands reduce the second binding energy. If the binding energy for the second ligand is reduced consistently throughout in a series of acetophenones, the binding energy of the first ligand can be estimate from the free energy changes for L$_2$Cu$^+$ by using a correction coefficient. Therefore, the CCAs and CCBs for the first and second ligands were calculated for a series of acetophenones. These results are summarized in Table 4. The f(CCA) and f(CCB) values that are the ratios of CCA[L$_2$Cu$^+$] to CCA[LCu$^+$] and CCB[L$_2$Cu$^+$] to CCB[LCu$^+$], respectively, decrease with increasing basicity of a ligand from 1.97 and 1.88 for p-CF$_3$ to 1.85 and 1.80 for p-NMe$_2$, respectively, indicating that the stronger base has the appreciably weaker second binding energy compared to the first one. In addition, the plot of the relative calculated binding energies with two ligands against the corresponding values for the first ligand (Fig. 3) shows that there is an excellent linear relationship with a slope 1.56 including all derivatives (Eq. (7)). A linear relationship having a similar slope is also obtained for CCAs (Eq. (8)).

$$\Delta\mathrm{CCB}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.56\,\Delta\mathrm{CCB}[\mathrm{LCu^+}]_{\mathrm{calc}} - 2.6 \quad (R^2 = 0.994) \tag{7}$$

$$\Delta\mathrm{CCA}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.51\,\Delta\mathrm{CCA}[\mathrm{LCu^+}]_{\mathrm{calc}} - 1.6 \quad (R^2 = 0.996) \tag{8}$$

For the calculated ΔCCBs and ΔCCAs using the B3LYP/6-31+G* optimized geometries, there are also excellent linear relationships with similar slopes.

$$\Delta\mathrm{CCB}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.46\,\Delta\mathrm{CCB}[\mathrm{LCu^+}]_{\mathrm{calc}} - 4.0 \quad (R^2 = 0.990) \tag{9}$$

$$\Delta\mathrm{CCA}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.54\,\Delta\mathrm{CCA}[\mathrm{LCu^+}]_{\mathrm{calc}} - 1.6 \quad (R^2 = 0.998) \tag{10}$$

Table 4
Calculated CCA and CCB values of substituted acetophenones[a]

Substituents in acetophenone	LCu$^+$		L$_2$Cu$^+$		f[CCA] [b]	f[CCB] [c]
	CCA	CCB	CCA	CCB		
p-NMe$_2$	270.1 (267.8)	235.7 (238.4)	499.4 (498.6)	424.8 (420.6)	1.85 (1.86)	1.80 (1.76)
p-NH$_2$	255.7 (254.6)	223.5 (228.6)	483.6 (479.3)	405.2 (407.1)	1.89 (1.88)	1.81 (1.78)
p-MeO	240.9 (241.7)	212.8 (212.9)	460.8 (461.1)	383.0 (383.6)	1.91 (1.91)	1.80 (1.80)
p-Me	231.6 (232.8)	201.7 (203.2)	447.4 (448.0)	373.4 (373.2)	1.93 (1.92)	1.85 (1.84)
m-Me	229.7 (230.8)	198.0 (198.8)	444.5 (445.1)	367.8 (371.6)	1.94 (1.93)	1.86 (1.87)
H	224.1 (225.1)	192.7 (194.5)	435.7 (436.3)	359.7 (362.7)	1.94 (1.94)	1.87 (1.86)
p-F	217.3 (218.4)	187.1 (188.5)	423.9 (424.5)	346.5 (351.8)	1.95 (1.94)	1.85 (1.87)
p-Cl	217.1 (217.4)	186.7 (187.0)	423.2 (422.4)	347.2 (344.6)	1.95 (1.94)	1.86 (1.84)
m-F	211.8 (213.5)	180.8 (182.6)	415.3 (416.8)	339.1 (339.8)	1.96 (1.95)	1.88 (1.86)
m-Cl	212.4 (213.1)	181.2 (182.1)	416.5 (416.1)	341.0 (339.7)	1.96 (1.95)	1.88 (1.87)
m-CF$_3$	203.2 (204.8)	172.7 (173.7)	400.7 (402.0)	324.5 (324.6)	1.97 (1.96)	1.88 (1.87)
p-CF$_3$	202.3 (203.7)	170.9 (172.5)	399.3 (400.3)	321.6 (325.6)	1.97 (1.97)	1.88 (1.89)

[a] Energies are calculated at MP2/6-311+G(2d,2p) using the optimized geometries at the B3LYP/6-311G. Thermal corrections obtained at the B3LYP/6-311G. No BSSE corrections. The values in the parentheses are based on the B3LYP/6-31+G* optimized geometries.

[b] f(CCA) = CCA[L$_2$Cu$^+$]/CCA[LCu$^+$].

[c] f(CCB) = CCB[L$_2$Cu$^+$]/CCB[LCu$^+$].

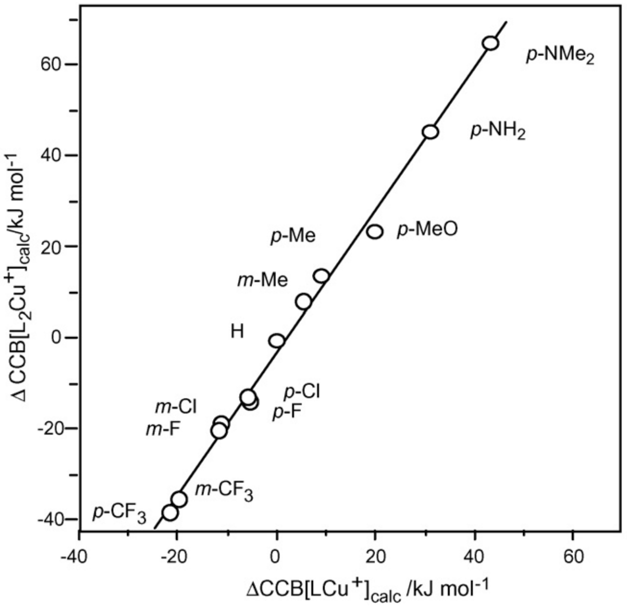


Fig. 3. Plot of ΔCCB[L_2Cu^+]$_{calc}$ vs. ΔCCB[LCu^+]$_{calc}$.

The slope of 1.5 is significantly smaller than the experimental value (1.9) for H_2O, NH_3, $(Me)_2O$, MeCN, and acetone noted above (Eq. (6)). This may indicate that the binding energy for the second ligand is reduced by the repulsive interaction between two ligands in the acetophenone system.

3.2.3. Natural charges and geometries for Lewis cation complexes

The group natural charges of the Cu^+ complexes derived using the natural population analysis (NPA) scheme at B3LYP/6-311G//B3LYP/6-311G are summarized in Table 4. For comparison the relevant complexes were also calculated at the same level of theory.

4. Discussion

4.1. Comparison between $\Delta CCB[L_2Cu^+]$ and $\Delta GB[LH^+]$

The relative ΔCCB[L_2Cu^+] values of acetophenones are plotted against the ΔGB values in Fig. 4. When the correlation is limited to *meta* substituents and *para* electron-withdrawing groups, there is an excellent linear correlation (Eq. (11)).

$$\Delta\text{CCB}[L_2Cu^+] = 1.24\,\Delta\text{GB} - 0.4 \quad (R^2 = 0.999) \qquad (11)$$

Using a linear relationship between the ΔCCB[L_2Cu^+]$_{calc}$ and ΔCCB[LCu^+]$_{calc}$, it is expected that there should be a linear relationship between ΔCCB for the monomeric adduct (LCu^+) and ΔGB with a slope of 0.83 (=1.24/1.5). The magnitude of 0.83 indicates that the substituent effect is considerably reduced in the copper adduct cation compared to that in the protonated system.

Fig. 4 shows another important fact that strong π-donor substituents have smaller stabilization effect in the Cu^+ adduct compared to the expected values from the linear relationship obtained for *meta* substituents and *para* electron-withdrawing groups. Closer examination of these deviations indicates that the stronger π-donor substituent shows the larger negative deviation and vice versa except for *p*-F and *p*-Cl. Such deviations of strong π-donor substituents have been observed whenever there is difference in the contribution of the resonance effect of π-donor substituent between two systems of interest [19,28]. Accordingly, the negative deviations suggest that the resonance effect of π-donor substituent is reduced in the Cu^+ adduct compared to that in the protonated ion. This is not unexpected result because the charge transfer from copper cation to acetophenone should be small (Table 5). It is interesting to examine whether the theoretical calculations reproduce such unique behavior of π-donor substituents in the stability of the Cu^+ adduct. Although the theoretical calculation of CCBs and CCAs at the present level of theory, MP2/6-311+G(2d,2p)//B3LYP/6-311G, does not perfectly reproduce the experimental values, it is possible to compare ΔCCB$_{calc}$[L_2Cu^+] with ΔGB$_{calc}$ calculated at the same

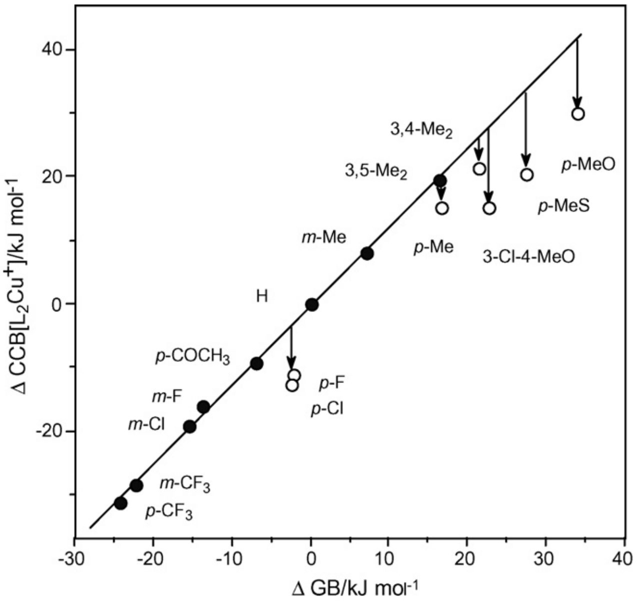


Fig. 4. Correlation between experimental ΔCCB[L_2Cu^+] and ΔGB.

Table 5
Selected bond distances (Å) and bond angles (degree) of acetophenone-M^+ complexes calculated at B3LYP/6-311G and group natural charges[a]

Lewis acids	M^+O8	C7O8	C1C7	M^+OC	Σq(Ph)[b]	Σq(M^+)[c]
Cu^+	1.810	1.286	1.451	133.6	0.205	0.905
Cu^{+}[d]	1.832	1.278	1.457	135.6	0.157	0.805
Li^+	1.708	1.278	1.457	171.4	0.169	0.984
Li^{+}[d]	1.763	1.270	1.465	170.5	0.131	0.957
Me_3Si^+	1.847	1.295	1.442	144.2	0.242	0.744
Me_3Ge^+	1.955	1.292	1.446	142.3	0.220	0.748
H^+	0.976	1.330	1.419	116.8	0.337	0.522
None	–	1.247	1.492	–	0.001	–

[a] Natural population analysis at B3LYP/6-311+G(2d,2p) using the B3LYP/6-311G optimized geometries.

[b] Summed natural charge of the phenyl moiety.

[c] Summed natural charge of the Lewis acid moiety.

[d] Dimeric complex, $[C_6H_5COCH_3]_2M^+$.

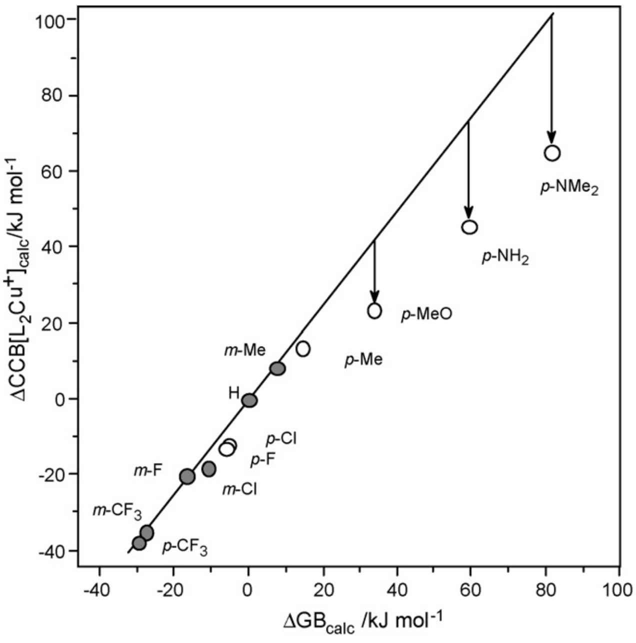


Fig. 5. Correlation between calculated $\Delta CCB[L_2Cu^+]_{calc}$ and the corresponding ΔGB_{calc}.

level of theory because factors resulting in differences between calculated and observed basicities may be canceled out.

Fig. 5 shows a plot of the calculated $\Delta CCB[L_2Cu^+]_{calc}$ values of acetophenones against the corresponding ΔGB_{calc}. It is found that non-conjugating substituents give a linear relationship with a slope of 1.24 similar to the experimental value and that *para* strong π-donor substituents clearly deviate downward from this line. This trend is in complete agreement with the experimental results as shown in Fig. 4. These negative deviations experimentally observed for strong π-donors should be intrinsic nature of the binding interaction between Cu^+ and ligands. In conclusion, these negative deviations indicate the reduced resonance effect in the Cu^+ adduct ions.

4.2. *Analysis of the substituent effect by Yukawa–Tsuno equation*

To describe quantitatively the contribution of the resonance effect involved in the stability of the Cu^+ adduct, the correlation analysis using the Yukawa–Tsuno (Y–T) equation (Eq. (12)) is useful [28]. Indeed, it has been applied successfully not only to GB but also to Li^+ [19], Me_3Si^+ [20], and Me_3Ge^+ basicities of acetophenones [21], and the obtained results have helped our understanding of the nature of the bond between Lewis acids and neutral ligands.

$$\Delta G = \rho(\sigma^\circ + r\,\Delta\bar{\sigma}_R^+) \tag{12}$$

where σ° and $\Delta\bar{\sigma}_R^+$ are the normal substituent constant and the resonance substituent constant, respectively, and r is the resonance demand parameter representing a degree of the π-delocalization of the positive charge into the aryl π-system. Application of the Y–T equation (Eq. (12)) to $\Delta CCB[L_2Cu^+]$ provides a ρ value of -56.2 ($kJ\,mol^{-1}\,\bar{\sigma}^{-1}$ unit) and an r value of 0.60 with satisfactory precision ($R^2 = 0.992$) as shown in Fig. 6 [29]. An excellent linear relationship between $\Delta CCB[L_2Cu^+]_{calc}$ and $\Delta CCB[LCu^+]_{calc}$ shown in Fig. 3 suggests that the magnitude of the r value is the same as in both complexes. Only difference in both substituent effects is the magnitude of ρ value. Therefore, the ρ of –37.5 can be assumed for the $\Delta CCB[LCu^+]$ for the first ligands by dividing a ρ of -56.2 by a factor of 1.5 as discussed above. The results of the Y–T analysis for Lewis cation basicities of acetophenones (Cu^+, Li^+, H^+, Me_3Si^+, and Me_3Ge^+) are summarized in Table 6. A comparison of the ρ values for a series of Lewis cation basicities in the acetophenone system shows that a ρ value decreases in the order for $H^+ > Me_3Si^+ > Me_3Ge^+ > Cu^+ > Li^+$. The ρ value is generally considered a measure of the magnitude of the charge developed at the benzylic carbon and/or of distance between the substituent and the reaction (charge) center. Since the ρ values obtained are not correlated with the size of Lewis cation, the calculated bond distance between Lewis cation and the oxygen

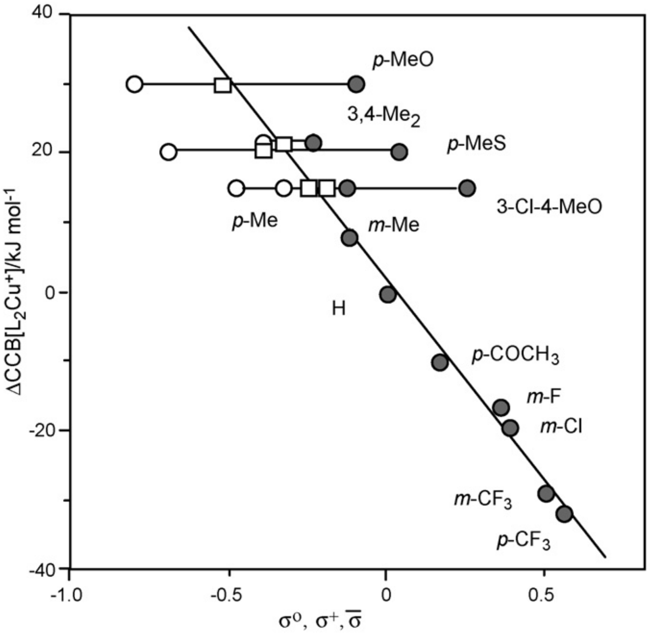


Fig. 6. The Y–T plot for $\Delta CCB[L_2Cu^+]$. (Closed circles) σ^o, (open circles) σ^+, (squares) apparent $\bar{\sigma}$ at $r = 0.60$.

Table 6
Correlation results of Y–T analysis for Lewis cation basicities of acetophenones

Lewis cation	$-\rho$[a]	r
H^+[b]	48.5	0.82
Me_3Si^+[c]	46.0	0.75
Me_3Ge^+[d]	40.6	0.71
Cu^+	37.5[e]	0.60
Li^+[f]	34.7[g]	0.49

[a] In $kJ\,mol^{-1}\,\bar{\sigma}^{-1}$ unit.
[b] Ref. [22].
[c] Ref. [20].
[d] Ref. [21].
[e] The estimated value for $\Delta CCB[LCu^+]$, see text.
[f] Ref. [19].
[g] The estimated value for $\Delta LCB[LLi^+]$, Ref. [19].

atom of the carbonyl group in the complex, the decreasing ρ value seems to indicate that the charge at the benzylic carbon decreases along this series, i.e., more positive charge is localized at the Lewis cation moiety of the adduct ions compared with that for protonation. The small ρ value for the Cu^+ complex would result from the ionic nature of the bond formed with Cu^+ compared to the protonation.

Similarly, the r value decreases in the same order as the ρ value. Since the r value represents the degree of charge-delocalization into the aromatic π-system [28], the moderate r value of 0.60 for the ΔCCB[LCu^+] reveals the existence of the π-delocalization of the positive charge into the aryl group, although charge transfer from copper cation to an acetophenone ligand must be much smaller than that in the protonated acetophenone. The group natural charges of the complexes given in Table 5 show that the natural charge of the phenyl moiety in the Cu^+ adduct is only 0.205 and 0.157 unit for monomeric and dimeric complexes, respectively, while that of the protonated ion is 0.337 unit. Supporting the change in the charge, the bond distance of C1C7 shortens by 0.041 Å on formation of the monomeric Cu^+ adduct and by 0.073 Å on protonation. On the contrary, the C7O8 bond lengthens by 0.039 Å on formation of the Cu^+ adduct and by 0.083 Å on protonation. Including other Lewis acid adducts and neutral acetophenone, there is a good linear relationship between the natural charge of the phenyl moiety and the C1C7 bond distance as shown in Fig. 7. A similar relationship is also observed for the C7O8 bond distance with the natural charge of the phenyl moiety (Eq. (14)). In addition, it is shown that the natural charge of the phenyl moiety decreases linearly with the increasing natural charge of the Lewis acid moiety (Eq. (15)).

$$\Sigma q_{\rm ph} = -4.63 R_{\rm C1C7} + 6.905 \quad (R^2 = 0.997) \tag{13}$$

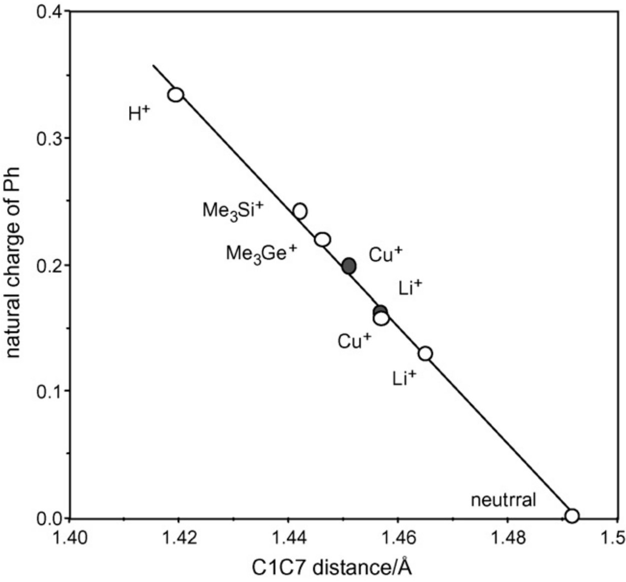


Fig. 7. Correlation between the group natural charge of the phenyl moiety and the C1C7 distance of the Lewis cation bound acetophenone. Closed circles indicate dimeric complexes.

$$\Sigma q_{\rm ph} = 3.98 R_{\rm C7O8} - 4.935 \quad (R^2 = 0.963) \tag{14}$$

$$\Sigma q_{\rm ph} = -0.364 \sum q_{\rm M} + 0.513 \quad (R^2 = 0.966) \tag{15}$$

These changes in bond distance and in the group charges with the variation of the Lewis acid are consistent with the change of the π-delocalization of the positive charge described by the r value.

Finally, it should be noted that the moderate π-delocalization described by $r = 0.60$ is observed for the Cu^+ complex, despite retaining the positive charge at Cu^+ (natural charge of Cu^+ of 0.91 and 0.81 unit in the monomeric and dimeric complexes, respectively). The apparent π-delocalization in the Cu^+ complex results from the polarization of the carbonyl bond caused by ionic interaction between Cu^+ and O=C. Since the π-orbitals of the double bond of the carbonyl group and the π-orbital of the benzene ring lie on the same plane, the positive charge at the carbonyl carbon atom can be stabilized by positive charge transfer to the benzene ring through π-interaction. In other words, the apparent π-delocalization in the Cu^+ complex results from the redistribution of the positive charge in the acetophenone moiety. Thus, the r value reflects the change in charge-redistribution in the ligand molecule as well as the charge transfer from a Lewis acid to a ligand. All these results show that Cu^+ complex has intermediate character between Li^+ and H^+. Accordingly, the smaller ρ value for the ΔCCB[LCu^+] than that for the ΔGB reflects intrinsic nature of the ionic bond forming with Cu^+. Considering the redistribution of the charge, the magnitude of the ρ value reveals a precise susceptibility of the substituent effect rather than the slope of an apparent linear relationship between CCBs and GBs, in which there are differences in factor contributing to their basicities. Therefore, a ρ value is a good measure of the ionic properties of the bond formed by Lewis cation as far as the substituent effect is properly analyzed. This is consistent with our previous results that the constant ρ values of −50 were observed for the GBs of a series of benzoyl compounds, ArCOR, in which the r value as well as the basicity of the parent compounds varies significantly with the polar effect of the R group, i.e., the r value decreases from 1.29 for α,α,α-trifluoroacetophenones (GB[Ar = C_6H_5] = 767.3 kJ mol^{-1}) [30], to 0.50 for methylbenzoates (819.6) [22], and to 0.23 for *N*,*N*-dimethylbenzamides (901.7) [31]. That is, the ρ value is less sensitive to the change in thermodynamic stability of the adduct ion as far as a covalent bond is formed with a very extensive positive charge transfer. In conclusion, the present analysis suggests that the use of the slope of a linear relationship between Lewis cation basicities and GBs for the study of the nature of the bond formed by Lewis acid must be limited within compounds having a similar framework. Otherwise, the apparent slopes will lead us to erroneous conclusions because of the different nature of Lewis cation–ligand interactions.

5. Conclusions

The copper cation basicities (CCB[L_2Cu^+]) were obtained for *m*- and *p*-substituted acetophenones in the gas phase based on the measurement of ligand-exchange equilibria of the type ${}^1L_2Cu^+ + 2{}^2L = {}^2L_2Cu^+ + 2{}^1L$ using an FT-ICR spectrometer. The substituent effects on CCB[L_2Cu^+] of acetophenone are characterized by a ρ value of −56.2 and an *r* value of 0.60 based on the analysis using the Yukawa–Tsuno equation. The ρ value of −37.5 for monomeric complex (LCu^+) could be evaluated from a ρ value for L_2Cu^+ by using a correction coefficient of 1.5 given by the theoretical calculations. In comparison with the corresponding results for other Lewis cation basicities it has been shown that the ρ value decreases in the order of H^+ (−48.5) > Me_3Si^+ (−46.0) > Me_3Ge^+ (−40.6) > Cu^+ (−37.5) > Li^+ (−34.7). The decrease in the ρ value indicates that the positive charge localized at the Lewis cation moiety of the adduct ion increases in this order, being in agreement with the change in the calculated natural charge. The smaller ρ value for the CCB than that for the protonation is consistent with ionic (ion–dipole interaction) nature of the bonding interaction between Cu^+ and the carbonyl oxygen atom. The ρ value of the Cu^+ complex larger than that for Li^+ complex suggests that the Cu^+ interaction involves somewhat covalent character compared to the Li^+ interaction. The *r* value also decreases in the same order. The moderate *r* value of 0.60 observed for the Cu^+ adduct ions may be due to the redistribution of the positive charge in the acetophenone moiety.

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