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Ab initio Density Functional Calculations on Copper(I)–CO_2 Coordinations[#]

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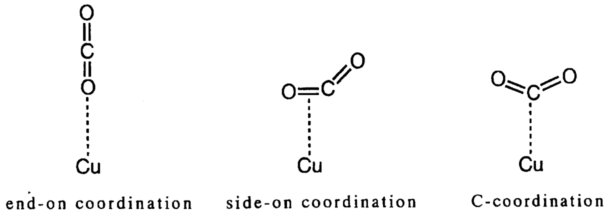
Full geometry optimizations have been carried out for the complex formations of Cu^+ and Cu(2,2′-bipyridine)$^+$ with CO_2 by using the density functional methods. The calculation demonstrated that the end-on coordination mode was mainly favored for all cases, while the binding of 2,2′-bipyridine (bpy) to $Cu(CO_2)^+$ largely labilized the end-on coordination mode and stabilized the in-plane side-on coordination mode. The detailed examination of the population analysis indicate that the coordination of bpy to Cu^+ weakens the electron donating character of CO_2 to Cu^+ and promotes the important participation of π-back-donative interaction from the metal ion to CO_2.

The study on the interaction between the metal ion and carbon dioxide is of interest from the view point of the activation of inert CO_2. It is well known that the carbon dioxide tends to form complexes with the transition metal ions in low oxidation state, in which the following three types, end-on, side-on, and C-coordinations, are considered as the bonding mode between the metal ion and CO_2, as shown in Scheme 1.[1)] The side-on coordination has been known in $[Ni\{P(C_6H_{11})_3\}_2(CO_2)]$,[2)] $[Nb(\eta^5\text{-}C_5H_4CH_3)_2\{CH_2Si(CH_3)_3\}(CO_2)]$,[3)] $[Mo\{P(CH_3)_3\}\{CNCH(CH_3)_2\}(CO_2)_2]$,[4)] and $[Mo(C_5H_5)_2(CO_2)]$.[5)] The C-coordination has been presumed in $[Ni\{P(C_6H_{11})_3\}_3(CO_2)]$,[6)] $[Ir\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2(CO_2)Cl]$,[7)] $[Rh(PR_nPh_{3-n})(CO_2)Cl]$,[8)] $[Rh\{o\text{-}C_6H_4(As(CH_3)_2)_2\}(CO_2)]Cl$,[9)] and $[Co(C_{22}H_{26}N_2O_2)K(CO_2)(C_4H_8O)]$.[10)] The structure of metal–CO_2 complex coordinated in the end-on mode has not been reported yet to our knowledge.[1)] Previously, Sakaki et al. reported the *ab initio* calculations of $[Ni(PH_3)_2(CO_2)]$ and $[Cu(PH_3)_2(CO_2)]$ with these three possible modes, end-on, side-on, and C-coordinations, and concluded that the former Ni(0) and latter Cu(I) complexes favored the side-on and end-on coordinations, respectively.[11)] However, there has been no experimental report on the Cu(I) complex with CO_2, although Cu(I) is in a low oxidation state and has the same electronic configuration as that of Ni(0). Therefore, it is very interesting to investigate theoretically any possibility on the Cu(I)–CO_2 complex formation in further detail and then to decide which of the three modes is the most favorable in this system. Studies on the full geometry optimizations for these systems have not been performed hitherto because of the extensively big magnitude in the calculation.



Scheme 1.

Recently, Andzelm et al. developed the DGauss program for quantum chemistry calculations, which made possible the accurate calculations of energy and geometry optimization at the same level as the Møller–Plesset second order perturbation methods (MP2) even in weak interaction such as hydrogen bonding.[12)] This method, therefore, is expected to give somewhat useful information on the coordinative interaction between Cu^+ and CO_2, although any unambiguous evidence on the existence of such a coordination have not been reported yet.

In this paper the Cu(I)–CO_2 complexes, $[Cu(CO_2)]^+$ and $[Cu(bpy)(CO_2)]^+$ (bpy=2,2′-bipyridine), with several coordination modes, as shown in Scheme 2, have been investigated by the *ab initio* density functional method. Such an attempt is very much interested, because this approach will give a useful guide to the synthesis of this sort of complexes.

Procedure

Computational Details. *Ab initio* calculations were carried out according to the density functional scheme by the use of DGauss program.[12a,12b)] The basis sets are Gaussian functions; (63321/5211/41) for copper, (721/51/1) for oxygen, nitrogen, and carbon atoms and (41/1) for hydrogen atom with the uncontracted auxiliary basis sets of (10/5/5), (7/3/3), and (4), respectively.[12b)] Geometry optimizations have been performed within the local spin density (LSD) approximation[12b,12c)] followed by self-consistent non-local corrections proposed by Becke[13)] and Perdew[14)] for the exchange and the correlation interactions, which can improve the results by the LSD approximation to a similar level to the MP2 method.[12b,12c)] The SCF convergence thresholds for the density and total energy are at 5×10^{-5} and 5×10^{-7} a. u., respectively. The conver-

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[#] This paper is dedicated to the late Professor Hiroshi Kato.

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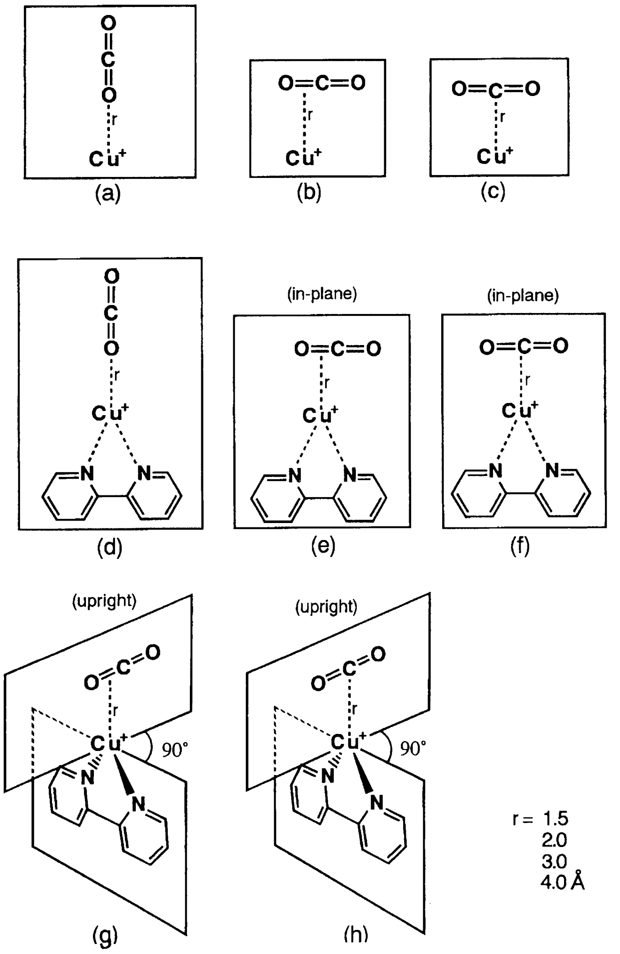

Scheme 2.

gence criterion for the largest gradient component is at 8×10^{-4} a. u./bohr. Any symmetrical restriction was not assumed during the calculations. All calculations were performed on the CRAY Y-MP supercomputers.

Initial Geometries. Computations of $[Cu(CO_2)]^+$ and $[Cu(bpy)(CO_2)]^+$ complexes were performed for three types of coordination, the side-on, end-on, and C-coordinations, respectively, as shown in Scheme 1. In all cases, the linear structure with the C=O bond length of 1.15 Å was employed as the starting geometry of CO_2. The bond lengths, 1.33, 1.32, and 0.95 Å, were used as the C–C, C–N, and C–H lengths in the bpy ligand. The initial Cu–N bond lengths in $[Cu(bpy)(CO_2)]^+$, not reported for this complex, was 1.96 Å which have been taken from the X-ray study of $[Cu(bpy)(CH_2{=}CH_2)]^+$.[15] The CO_2 located at the position of 2.0 Å from Cu^+ ion, in each case as shown in Scheme 2. The calculations of $[Cu(bpy)(CO_2)]^+$ were performed for two possible initial geometries; in one of which the OCO′ molecule lies in the same plane with that of bpy (in-plane) and in the other the former is perpendicular to the latter (upright).

Results and Discussion

Geometry Optimization. At the begining, the full geometry optimization of CO_2 was performed, which converged to the linear structure with the C=O bond length of 1.183 Å. The full geometry optimizations for eight possible coordination modes shown in Scheme 2 gave five probable geometries of $[Cu(CO_2)]^+$ and $[Cu(bpy)(CO_2)]^+$, as illustrated in Fig. 1, together with the interatomic distances and angles. Although these geometries were obtained when the Cu^+–CO_2 distance of 2.0 Å was employed as the starting geometry, they were applied also for those of 1.5, 3.0, and 4.0 Å. Their results, however, converged to the almost same geometries as those obtained here. The total energies for their optimized structures are listed in Table 1, together with the binding energies between the Cu(I) complexes and CO_2.

The optimization of $[Cu(CO_2)]^+$ converged to two types of end-on coordination mode for all three cases ((a)—(c) in Scheme 2); linear and bent coordinations ((a) and (b)) as shown in Fig. 1, suggesting that the Cu^+ ion stabilizes the end-on mode in the complexation with CO_2, in agreement with that reported by Sakaki et al.[11] The optimization, when started from the linear type end-on coordination mode, unchanged the mode almost as such, but that from the side-on mode resulted

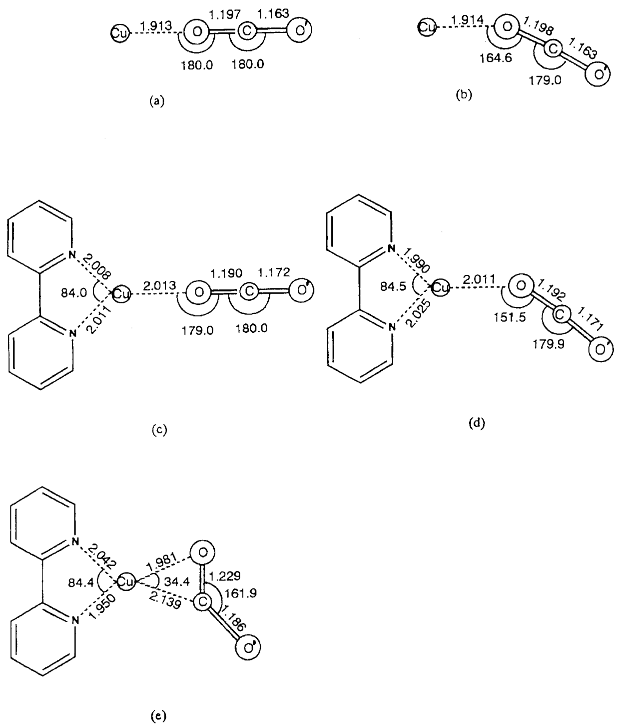

Fig. 1. Optimized structures of $[Cu(CO)_2]^+$ and $[Cu(bpy)(CO)_2]^+$. Interatomic distances and angles are given in Å and degree units, respectively. In each case of (c), (d), and (e), all the atoms optimized lie on the almost same plane.

Table 1. Total Energies of the Cu(I)–CO_2 Complexes and Binding Energies between the Copper(I) Complex and CO_2[a)]

	$[Cu(CO_2)]^+$ linear end-on	$[Cu(CO_2)]^+$ bent end-on	$[Cu(CO_2)]^{+b)}$ side-on	$[Cu(bpy)(CO_2)]^+$ lenear end-on	$[Cu(bpy)(CO_2)]^+$ bent end-on	$[Cu(bpy)(CO_2)]^+$ side-on
Total energy /a.u.	−1828.8102	−1828.8106	−1828.7827	−2324.4500	−2324.4498	−2324.4461
Binding energy /kcal mol^{-1}	27.0	27.3	9.8	14.1	13.9	11.6

a) The values of −188.6392 and −2135.7884 a. u. were used as the energy of the CO_2 and $Cu(bpy)^+$ ion, which were calculated by the same method as performed here. b) The energies of this complex were calculated using the geometry of the side-on $[Cu(bpy)(CO_2)]^+$ structure optimized.

in its change to the bent type end-on mode. In both cases, the O=C=O′ bonds were almost linear. The total energies for these two coordination types and their binding energies between the metal complexes and CO_2 are not significantly distinguished within ±0.3 kcal mol^{-1}, as given in Table 1. Their geometrical parameters are also the almost same except the difference between the Cu···O=C angles. Both C=O distances, 1.197 and 1.198 Å, are slightly elongated by the coordination to Cu^+ in comparison with that of the free CO_2 optimized. The Cu···O distances in the two types are in good agreement with the Cu(I)···oxygen bond reported hitherto.[16)] On the other hand, the optimization from the C-coordination mode with the Cu···CO_2 separation of 2.0 Å was energetically locally minimized to the almost same coordination mode with the slight bending of O=C=O′, but the total energy, −1828.7721 a. u., was larger than the other two types and the binding energy, 3.5 kcal mol^{-1}, was also too small to fix the CO_2 to Cu^+ in comparison with those of the other two types.

The optimizations of $[Cu(bpy)(CO_2)]^+$ converged to three coordination types ((c)—(e)), as shown in Fig. 1; two of them being end-on coordination modes (linear and bent coordinations) and the other one being side-on coordination mode. Interestingly, the simultaneous bindings of bpy and CO_2 to Cu^+ labilized the end-on coordination mode and stabilized the in-plane coordination mode, which resulted in that their total energies and the binding energies of CO_2 with $Cu(bpy)^+$ were comparable to within ±2 kcal mol^{-1} each other as shown in Table 1. The optimization from the linear type end-on coordination mode almost unchanged as such, but those from the in-plane and upright C-coordination and upright side-on coordination modes resulted in their change to the bent type end-on mode. That from the in-plane side-on coordination maintained as it was, although the total energy was larger by ca. 2 kcal mol^{-1} in the side-on mode in comparison with the end-on coordination mode. Such a side-on coordination mode could not been formed through the optimization for all cases in the $[Cu(CO_2)]^+$ complex without bpy. The geometry parameters in both of the end-on types are also almost the same except the difference between their Cu···O=C angles. The Cu···O distances, 2.011 and 2.013 Å, are elongated by the coordination of bpy to $[Cu(CO_2)]^+$. In the bent type end-on coordination, the Cu···O=C angle is reduced from 164.6° to 151.5° by the binding of bpy. Both C=O bond lengths, 1.190 and 1.192 Å, are also slightly elongated by the coordination to Cu(I). In both types the O=C=O′ bonds are almost linear. On the other hand, the fact that the binding of bpy to $[Cu(CO_2)]^+$ has stabilized the side-on coordination mode indicates the presence of a π-back donative bonding between dπ(Cu(I)) and π*(O=C), which is supported by the significant elongation of C=O bond, 1.299 Å. The Cu···O distance is shorter than the Cu···C one, suggesting also the participation of an electrostatic interaction between Cu(I) and O. The O=C=O′ angle was optimized to 161.9°, which is larger than that for $[Ni(PH_3)_2(CO_2)]$ reported by Sakaki et al.[11)] The small bending in the Cu(I) complexes may suggest that the π-back donative interaction in the Cu(I) complex is weaker in comparison with that in the Ni(0) complex. In order to evaluate the stability of the side-on coordination mode upon the binding of bpy to $Cu(CO_2)^+$, the total energy for $Cu(CO_2)^+$ with side-on coordination mode was calculated using the geometry of the side-on type $[Cu(bpy)(CO_2)]^+$ ((e) in Fig. 1), which was less stable by ca. 17 kcal mol^{-1} in comparison with the end-on type $Cu(CO_2)^+$ complexes, as demonstrated in Table 1. Although the side-on type $[Cu(bpy)(CO_2)]^+$ is less stable by ca. 2 kcal mol^{-1} than the end-on type ones, the instability is negligibly small in comparison with that in the $Cu(CO_2)^+$ complexes. These results indicate that the coordination of bpy to Cu(I) promotes the fixation of CO_2 in the side-on mode, which is the first proposal of this work.

The Nature of Coordination Bond. Previously, Sakaki et al. reported that the $[Ni(PH_3)_2(CO_2)]$ complex favored the side-on mode, whereas the $[Cu(PH_3)_2(CO_2)]^+$ complex was stabilized by the end-on mode and did not prefer the side-on coordination.[11)] The results obtained in the present investigation show that the end-on mode is mainly preferred in the Cu(I) complexes, and furthermore, the side-on mode is also favored by the simultaneous coordination of bpy. The Mulliken populations of $[Cu(CO_2)]^+$ and $[Cu(bpy)(CO_2)]^+$ are given in Table 2.

The total and binding energies for the linear and bent type end-on modes, as shown in Table 1, are almost

Table 2. Atomic and Overlap Electron Populations for Cu(I)–CO_2 Complexes[a)]

	Cu–CO_2		Cu(bpy)–CO_2		
	Linear end-on	Bent end-on	Linear end-on	Bent end-on	Side-on
Cu	28.13	28.13	28.52	28.52	28.60
s	6.23	6.24	6.50	6.50	6.54
p	12.07	12.07	12.36	12.36	12.50
d	9.82	9.82	9.66	9.68	9.56
CO_2	21.87	21.87	21.99	21.97	21.98
s(O)	3.69	3.70	3.71	3.73	3.80
p(O)	4.57	4.57	4.50	4.49	4.40
s(C)	2.85	2.85	2.89	2.89	2.93
p(C)	2.45	2.44	2.52	2.50	2.46
s(O′)	3.78	3.77	3.77	3.77	3.77
p(O′)	4.27	4.27	4.34	4.33	4.33
bpy	—	—	81.49	81.51	81.42
Cu–C	−0.10	−0.10	−0.15	−0.17	0.04
Cu–O	0.17	0.19	0.03	0.08	0.21
Cu–O′	0.04	0.04	0.01	0.01	−0.03
Cu–N1	—	—	0.49	0.48	0.44
Cu–N2	—	—	0.49	0.48	0.53

a) O and O′ atoms in CO_2 denote the atoms coordinating and non-coordinating to Cu^+, respectively.

the same in the respective case of $[Cu(CO_2)]^+$ and $[Cu(bpy)(CO_2)]^+$. The Mulliken populations (Table 2) suggest an important contribution of the electrostatic interaction between Cu(I) and the O atom of CO_2; the CO_2 atomic populations are larger on O atom than O′ atom, especially on their p-orbitals. The coordination of bpy, however, reduces the electron population on the p-orbitals of the coordinated O atoms, suggesting the reduction of the electrostatic interaction between Cu^+ and O atom.

On the other hand, the side-on coordination structure was locally minimized in $[Cu(bpy)(CO_2)]^+$, although the total energy is slightly smaller than those with two end-on modes. The electron population on O atoms are also large, although in a reasonable degree. These facts mean that not only the electrostatic interaction but also the σ-donative and π-back denative interactions contribute to this coordination mode. It is also seen on the Cu and CO_2 atomic populations. The electron population on the Cu p-orbital increases and that on the Cu 3d orbital decreases, as shown in Table 2, which are due to σ-donation from CO_2 to Cu and π-back donation from Cu to CO_2. The large electron populations in Cu–C and Cu–O bond also suggest such interactions.

Conclusion

In this paper the Cu(I)–CO_2 complexes, $[Cu(CO_2)]^+$ and $[Cu(bpy)(CO_2)]^+$ (bpy=2,2′-bipyridine), with several coordination modes have been investigated by the *ab initio* density functional method. The full geometry optimizations for these complexes demonstrated that the end-on coordination mode was mainly favored for all cases, while the binding of bpy to $[Cu(CO_2)]^+$ largely labilized the end-on coordination mode and stabilized the in-plane side-on coordination mode. The detailed examination of the calculation results indicated that the coordination of bpy to Cu^+ weakened the electron donating character of CO_2 in the end-on coordination mode and promoted the important participation of the π-back-donative interaction from the metal ion to CO_2 in the side-on coordination mode. The two types of the end-on coordination, linear and bent ones, are energetically likely favored. In the $[Cu(bpy)(CO_2)]^+$ complex, the side-on mode was formed, although the total energy was not so stable in that for the end-on mode. In this case, the distortion of CO_2 appeared, whose O=C=O′ bond angle, 161°, was large in comparison with the experimental value reported for $[Ni\{P(C_6H_{11})_3\}_2(CO_2)]$[2)] and $[Ni\{P(C_6H_{11})_3\}_2(CO_2)]$.[6)] These results indicate that the end-on mode is favored in the Cu(I) complex, whereas the binding of bpy to Cu^+ stabilizes the side-on mode; the coordination of bpy to $Cu(CO_2)^+$ make possible to form both of end-on and side-on coordination modes. Our ultimate goal is the activation of carbon dioxide, which may be expected in the activation process of carbon dioxide through the synthesis of the Cu(I)–CO_2 complex in the succeeding investigation.

The calculations were partly carried out at the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

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