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STRUCTURAL STUDIES OF COPPER(I) COMPLEXES WITH ETHYLENE. CRYSTAL STRUCTURES OF [Cu(2,2′-BIPYRIDINE)(ETHYLENE)]ClO_4 AND [Cu(1,10-PHENANTHROLINE)(ETHYLENE)]ClO_4

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Summary

The crystal structures of the complexes [Cu(2,2′-bipyridine)(ethylene)]ClO_4 (I) and [Cu(1,10-phenanthroline)(ethylene)]ClO_4 (II) have been determined from X-ray diffraction studies. Complex I crystallizes in the triclinic space group, $P\bar{1}$, with four molecules in a unit cell of dimensions a 10.657(1), b 6.998(1), c 18.251(2) Å, α 91.05(1), β 93.35(1), and γ 84.97(1)°. Complex II crystallizes in the monoclinic space group, $P2_1/a$, with four molecules in a unit cell of dimensions a 19.981(5), b 10.904(2), c 6.955(1) Å, and β 103.90(2)°. Both structures were solved by heavy-atom methods, and refined by block-diagonal least-squares methods. The final R-values for I and II were 0.044 for 2225 observed reflections for I and 0.066 for 2005 observed reflections for II. In both crystals, the Cu^I ion is coordinated to two nitrogen atoms of 2,2′-bipyridine or 1,10-phenanthroline, and two carbon atoms of ethylene in an approximately planar form. The C–C bond distances of the coordinated ethylene molecules, 1.360(13) and 1.346(18) Å for I and 1.361(22) Å for II, do not show marked lengthening compared with that for free ethylene, and may be explained by $d_\pi(Cu) \rightarrow d_\pi$(ethylene) back-bonding between the Cu $3d_\pi$ orbital and the Rydberg $3d_\pi$ orbital of the ethylene molecule.

Introduction

Ethylene is known to be the most simple plant hormone, and causes seeds to sprout, flowers to bloom, fruit to ripen and fall off, and leaves and petals to shrivel and turn brown [1]. Studies on its activity in plants showed that the presence of a metal ion was required at the ethylene receptor site [2]. Recently, on the basis of the spectroscopic and structural studies of Cu^I-ethylene [3], Thompson et al. proposed

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that a Cu^I ion may play a critical role as the receptor site for the plant hormone ethylene. The coordination mode of ethylene to Cu^I ions in Cu^I-ethylene complexes, (ethylene)(di-2-pyridylamine)copper(I) perchlorate, chloride[hydrokis(1-pyrazolyl) borato](ethylene)dicopper, and [hydrotris(3,5-dimethyl-1-pyrazolyl)borato](ethylene)copper(I) seems to suggest that the nature of the Cu^I–ethylene bonding is dominated by σ-donation from the ethylene molecule to the Cu^I ion rather than by the π-back-donation from the Cu^I ion to the ethylene π^* orbital. Munakata et al., however, recently showed the importance of π-back-donation from their studies on the formation constants and ^1H NMR of several Cu^I–ethylene complexes [4].

Here, the X-ray structures of $[Cu(bpy)(ethylene)]ClO_4$ (I) and $[Cu(phen)(ethylene)]ClO_4$ (II) complexes with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) as the bidentate ligand (biL) are described, and the nature of Cu^I–ethylene bonding is discussed.

Experimental

Preparation of $[Cu(bpy)(C_2H_4)]ClO_4$ (I) and $[Cu(phen)(C_2H_4)]ClO_4$ (II)

Complex I was prepared by stirring an acetone solution of [tetrakis(acetonitrile)copper(I)] perchlorate and 2,2′-bipyridine under ethylene [4]. A white crystalline product was obtained. White crystals of II were prepared in the same manner as for I [4].

X-ray data collection and structure solution and refinement

Crystals suitable for diffraction studies were obtained for both compounds by cooling an ethylene-saturated acetone solution of the complex. Preliminary X-ray diffraction studies established a triclinic unit cell containing four chemical units for I and a monoclinic unit cell containing four chemical units for II. The crystal data are listed in Table 1.

Crystals with dimensions 0.1 × 0.2 × 0.2 mm for I and 0.1 × 0.2 × 0.3 mm for II were mounted on a Rigaku AFC-5 diffractometer with graphite-monochromated

TABLE 1

CRYSTAL DATA FOR $[Cu(bpy)(C_2H_4)]ClO_4$ (I) AND $[Cu(phen)(C_2H_4)]ClO_4$ (II)

	I	II
Formula	$CuClC_{12}H_{12}N_2O_4$	$CuClC_{14}H_{12}N_2O_4$
Mol. weight	347.26	371.26
Crystal system	triclinic	monoclinic
Space group	$p\bar{1}$	$p2_1/a$
a (Å)	10.657(1)	19.981(5)
b (Å)	6.998(1)	10.904(2)
c (Å)	18.251(2)	6.955(1)
α (°)	91.05(1)	90
β (°)	93.35(1)	103.90(2)
γ (°)	84.97(1)	90
V (Å^3)	1353.4	1470.9
Z	4	4
D_c (g/cm^3)	1.705	1.677
No. of unique data used	2225	2005

Cu-K_α radiation ($\bar{\lambda}$ 1.54178 Å). The crystal of I had a tendency to twin across the *ab*-plane. The crystal used for the observation included a small percentage of counterpart spots in the intensity. The intensity data in the range $2\theta < 120°$ were collected in the ω–2θ scan mode with a 0.8° scan range and a scan rate of 0.4° min^{-1}. Three reflections were monitored every 56 reflections. There was no significant variation of the intensities during data collection. The intensity data were

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS OF [Cu(bpy)(C_2H_4)]ClO_4(I) (with estimated standard deviations in parentheses)

Atom	*x*	*y*	*z*	B_{eq} ^{a} (Å^2)
Cu(1)	0.0198(1)	0.2518(1)	0.1033(1)	3.45
Cu(2)	0.5114(8)	0.2519(1)	0.6034(1)	2.78
Cl(1)	−0.0193(2)	0.7511(3)	0.3284(1)	4.02
Cl(2)	0.4864(2)	0.7312(3)	0.8286(1)	4.73
C(1)	0.0550(7)	0.2726(11)	−0.0497(4)	3.47
C(2)	0.1137(6)	0.2847(10)	−0.1129(4)	2.71
C(3)	0.2445(8)	0.3287(12)	−0.1126(5)	4.15
C(4)	0.3012(8)	0.3531(12)	−0.0424(5)	4.03
C(5)	0.2484(9)	0.3393(14)	0.0201(6)	4.98
C(6)	−0.0828(7)	0.2299(11)	−0.0420(4)	3.65
C(7)	−0.1634(8)	0.2081(14)	−0.1036(6)	5.00
C(8)	−0.2843(9)	0.1595(14)	−0.0907(6)	5.24
C(9)	−0.3263(9)	0.1543(14)	−0.0247(6)	5.21
C(10)	−0.2381(6)	0.1742(9)	0.0311(4)	2.39
C(11)	0.4243(6)	0.2241(9)	0.4552(4)	2.48
C(12)	0.3463(7)	0.2109(11)	0.3936(4)	3.51
C(13)	0.2228(7)	0.1758(11)	0.3982(4)	3.55
C(14)	0.1833(7)	0.1456(11)	0.4687(4)	3.46
C(15)	0.2515(10)	0.1591(16)	0.5337(6)	5.79
C(16)	0.5639(6)	0.2716(10)	0.4535(4)	2.85
C(17)	0.6306(9)	0.2942(16)	0.3919(6)	5.75
C(18)	0.7522(11)	0.3339(19)	0.3914(7)	7.07
C(19)	0.8082(10)	0.3457(16)	0.4602(7)	5.99
C(20)	0.7420(7)	0.3258(12)	0.5224(5)	3.82
C(21)	−0.0305(9)	0.2285(14)	0.2080(6)	5.20
C(22)	0.0936(8)	0.2600(12)	0.2076(5)	4.06
C(23)	0.4625(11)	0.2215(15)	0.7052(7)	6.75
C(24)	0.5808(12)	0.2742(18)	0.7037(8)	7.14
N(1)	0.1243(7)	0.2935(12)	0.0163(5)	3.16
N(2)	−0.1174(5)	0.2093(7)	0.0265(3)	2.06
N(3)	0.3743(8)	0.2000(12)	0.5280(5)	3.02
N(4)	0.6193(5)	0.2893(7)	0.5216(3)	2.27
O(1)	−0.0375(6)	0.9300(11)	0.3668(4)	5.98
O(2)	0.0031(9)	0.6076(14)	0.3837(6)	9.22
O(3)	−0.1306(7)	0.6954(11)	0.2929(5)	6.36
O(4)	0.0811(5)	0.7580(8)	0.2805(3)	4.30
O(5)	0.3647(7)	0.7521(12)	0.7897(5)	7.35
O(6)	0.5858(12)	0.7552(21)	0.7553(8)	12.89
O(7)	0.4912(7)	0.8713(11)	0.8883(5)	6.73
O(8)	0.5208(8)	0.5574(12)	0.8711(5)	7.48

^{a} B_{eq} is the equivalent isotropic temperature factor as defined by Hamilton [13].

converted to F_0 data in the usual manner. Absorption correction was not applied (μ 21.75 for I and 19.79 cm^{-1} for II). The standard deviations, $\sigma(F_o)$, were estimated by counting statics. Total numbers of independent reflections with $F_o \geqq 3\sigma$ (F_o) were 2225 for I and 2005 for II.

The structures were solved by the heavy-atom method and refined by block-diagonal least-squares refinement. In the least-squares refinements, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where $w = 1/\sigma^2(F_o)$. Atomic scattering factors [5a] and anomalous dispersion terms [5b] were taken from International Tables for X-Ray Crystallography, Vol. IV. Hydrogen atoms were included as a fixed contribution in the last cycle; their positions were assumed to be in accord with the idealized geometry (C–H 1.00 Å), and their temperature factors were assumed to be isotropic (B 8.00 Å). The final R and R_w values were 0.044 and 0.077 for I and 0.066 and 0.112 for II. The final difference Fourier maps showed no peaks greater than 0.5 for I and 0.4 e/Å^3 for II, with most of the largest peaks occurring around the copper atoms. All calculations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY [6].

The final positional and isotropic temperature factors of the non-hydrogen atoms are listed in Table 2 for I and Table 3 for II.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS OF [Cu(phen)(C_2H_4)]ClO_4 (II) (with estimated standard deviations in parentheses)

Atom	x	y	z	B_{eq} [a] (Å^2)
Cu	0.6427(1)	0.1013(2)	0.8759(2)	4.05
Cl	0.6755(1)	0.4472(3)	0.4690(5)	4.35
C(1)	0.5000(5)	0.0774(10)	0.7771(14)	3.28
C(2)	0.4277(5)	0.0970(11)	0.7421(15)	4.04
C(3)	0.4083(6)	0.2213(14)	0.7678(18)	5.56
C(4)	0.4552(7)	0.3117(12)	0.8214(19)	5.58
C(5)	0.5253(7)	0.2839(11)	0.8556(18)	5.02
C(6)	0.5255(5)	−0.0441(9)	0.7496(14)	3.10
C(7)	0.4797(5)	−0.1436(10)	0.6905(15)	3.76
C(8)	0.5080(6)	−0.2585(10)	0.6650(17)	4.53
C(9)	0.5775(7)	−0.2712(11)	0.6965(18)	4.88
C(10)	0.6193(6)	−0.1686(12)	0.7536(17)	4.51
C(11)	0.3829(5)	−0.0055(13)	0.6826(18)	4.81
C(12)	0.4057(6)	−0.1196(12)	0.6571(18)	4.86
C(13)	0.7188(6)	0.2188(14)	0.9879(22)	6.13
C(14)	0.7467(6)	0.1076(15)	0.9645(23)	6.46
N(1)	0.5475(4)	0.1707(8)	0.8326(13)	3.72
N(2)	0.5956(4)	−0.0576(8)	0.7826(12)	3.32
O(1)	0.6381(5)	0.4351(9)	0.2659(15)	6.88
O(2)	0.7053(5)	0.5656(8)	0.4986(16)	6.32
O(3)	0.7267(5)	0.3554(9)	0.5133(20)	8.48
O(4)	0.6291(5)	0.4341(10)	0.5978(17)	7.77

[a] B_{eq} is the equivalent isotropic temperature factor as defined by Hamilton [13].

Results

Structure of [Cu(bpy)(C_2H_4)]ClO_4 (I)

The crystal structure of I is depicted in Fig. 1. The unit cell contains two independent pairs of Cu(bpy)(C_2H_4) cationic groups and four well-separated perchlorate anions; the shortest Cu–O distance is 4.76 Å. The two independent cationic groups have nearly similar structure. The copper atom of each group is coordinated to two nitrogen atoms of the bpy molecule and two carbon atoms of the ethylene molecule, as shown in Fig. 2. The copper, two nitrogen and two carbon atoms are planar to within 0.03 Å. The dihedral angles between the planes defined by the copper and two nitrogen atoms of the bpy molecule, and by the copper and two carbon atoms of ethylene molecule are 3.4 and 3.4°. The two planar bpy moieties related by a center of symmetry were packed in parallel, and the interplanar distance between the mean planes of the bpy moieties is 3.31 Å.

Selected bond distances and angles are presented in Table 4. The Cu–N bond distances are typical of three-coordinate Cu^I complexes (1.93–2.16 Å) [3,7] and the Cu–C bond distances fall in the range (1.93–2.07 Å) observed previously [3]. The C–C bond distances of the coordinated ethylene molecule, 1.360(13) and 1.346(18) Å, are comparable with 1.359(7) Å for (ethylene)(di-2-pyridylamine)copper(I) perchlorate [3b] and 1.347(5) Å for chloro[hydrokis(1-pyrazolyl)borato] (ethylene)dicopper previously reported [3c]. These distances are, however, only slightly larger than the 1.337(2) Å for the free ethylene molecule [8], and 1.329(9) Å for [hydrokis(3,5-dimethyl-1-pyrazolyl)borato](ethylene)copper(I) previously reported [3b].

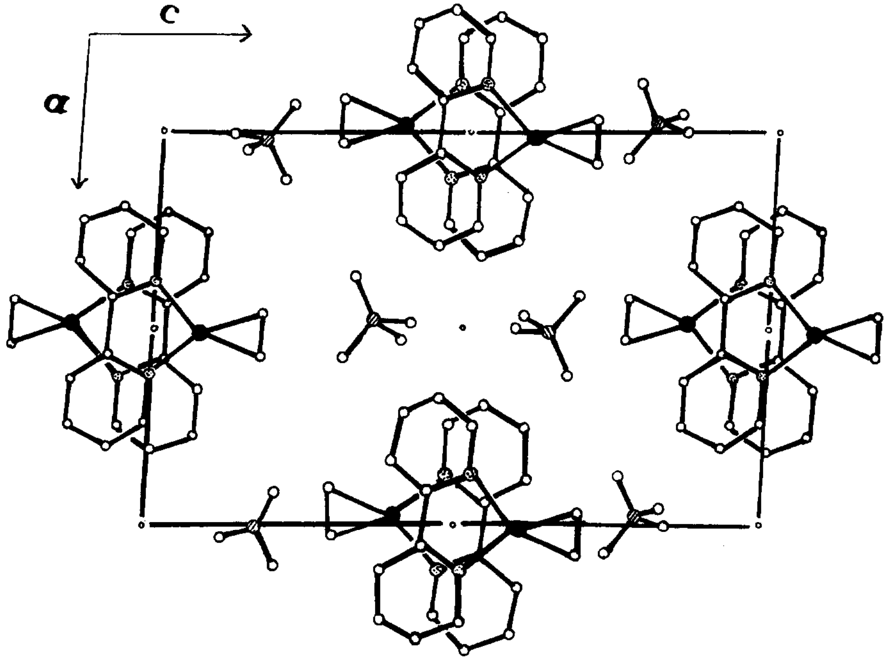
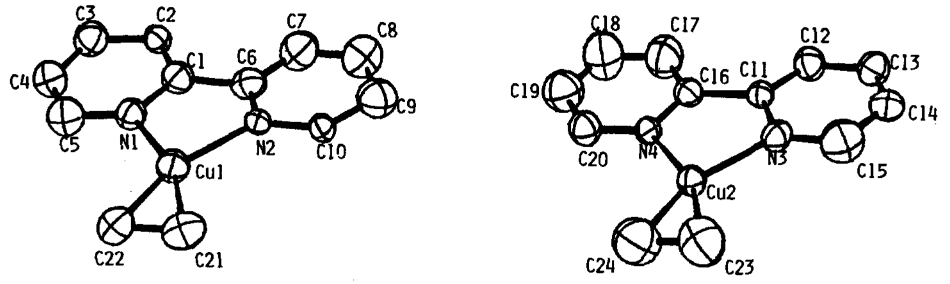


Fig. 1. The crystal structure of [Cu(bpy)(C_2H_4)]ClO_4 (I) along the *b* axis.



(a) (b)

Fig. 2. The two independent molecular structures of $[Cu(bpy)(C_2H_4)]ClO_4$ (I), (a) and (b), showing the atom labeling. The thermal ellipsoids are drawn at the 50% probability level.

Structure of $[Cu(phen)(C_2H_4)]ClO_4$ *(II)*

The crystal structure of II is depicted in Fig. 3. The unit cell contains four $Cu(phen)(C_2H_4)$ cationic groups and four well-separated perchlorate anions; the shortest Cu–O distance is 4.09 Å. The copper atom of each group is coordinated to two nitrogen atoms of the phen molecule, and to an ethylene molecule in a trigonal-planar arrangement, as shown in Fig. 4. The overall structure is similar to that for I. The copper, two nitrogen and two carbon atoms are planar to within 0.03 Å. The dihedral angle between the planes defined by the copper and two nitrogen atoms of the phen molecule, and by the copper and the two carbon atoms of ethylene is 2.5°. The two planar phen moieties are related by a center of symmetry, as shown in Fig. 3, and thus are parallel to each other. The interplanar distance between the mean planes of the phen moieties is 3.35 Å.

Selected bond distances and angles for II (see Table 5) are nearly equal to the corresponding distances and angles for I. The C–C bond distance of the coordinated ethylene, 1.361(22) Å, is essentially the same as that in I.

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[Cu(bpy)(C_2H_4)]ClO_4$ (I) [a]

Cu(1)–N(1)	2.032(9)	Cu(2)–N(3)	2.000(9)
Cu(1)–N(2)	2.003(5)	Cu(2)–N(4)	1.972(6)
Cu(1)–C(21)	2.028(11)	Cu(2)–C(23)	1.979(13)
Cu(1)–C(22)	2.019(9)	Cu(2)–C(24)	1.943(14)
C(21)–C(22)	1.360(13)	C(23)–C(24)	1.346(18)
N(1)–Cu(1)–N(2)	84.4(3)	N(3)–Cu(2)–N(4)	87.5(3)
N(1)–Cu(1)–C(21)	161.1(4)	N(1)–Cu(1)–C(22)	121.8(3)
N(2)–Cu(1)–C(21)	114.5(3)	N(2)–Cu(1)–C(22)	153.7(3)
N(3)–Cu(2)–C(23)	113.1(4)	N(3)–Cu(2)–C(24)	153.2(5)
N(4)–Cu(2)–C(23)	159.2(4)	N(4)–Cu(2)–C(24)	119.3(4)
N(1)–Cu(1)–C_t [b]	141.4(4)	N(2)–Cu(1)–C_t [b]	133.1(3)
N(3)–Cu(2)–C_t' [b]	133.1(4)	N(4)–Cu(2)–C_t' [b]	139.3(4)
C(21)–Cu(1)–C(22)	39.3(4)	C(23)–Cu(2)–C(24)	40.1(5)

[a] Estimated standard deviations are in parentheses. [b] C_t and C_t' represent the midpoints of the C(21)–C(22) and C(23)–C(24) bonds, respectively.

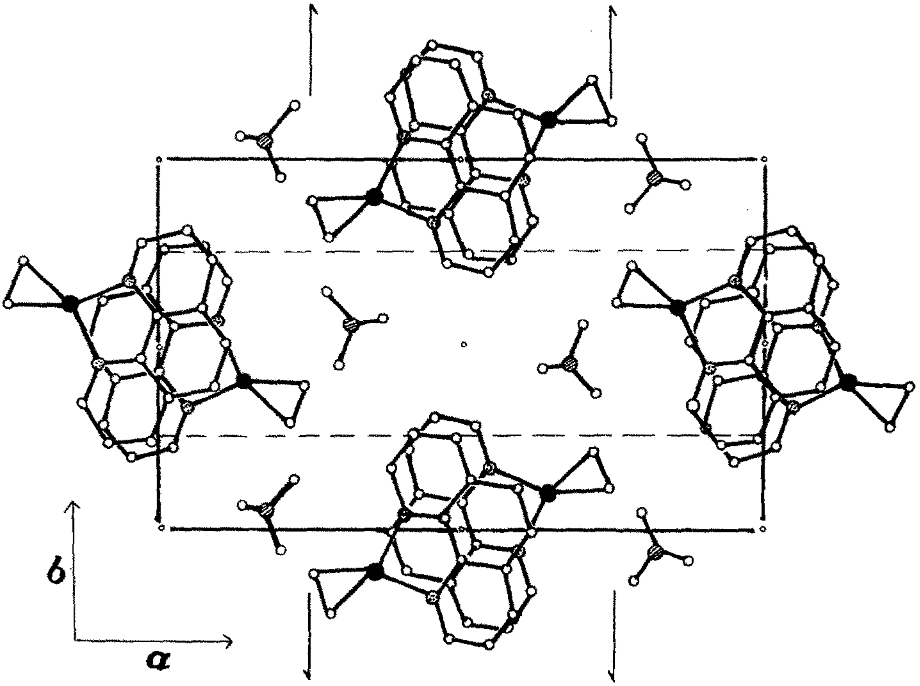


Fig. 3. The crystal structure of [Cu(phen)(C_2H_4)]ClO_4 (II) along the *c* axis.

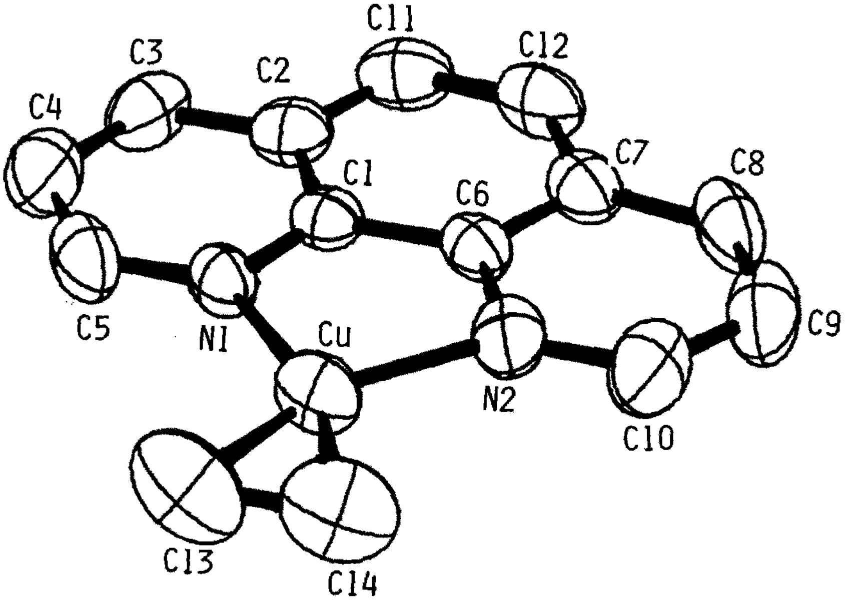


Fig. 4. The molecular structure of [Cu(phen)(C_2H_4)]ClO_4 (II) showing the atom labeling. The thermal ellipsoids are drawn at the 50% probability level.

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $[Cu(phen)(C_2H_4)]ClO_4$ (II) [a]

Cu-N(1)	2.002(8)	Cu-N(2)	2.004(9)
Cu-C(13)	1.998(13)	Cu-C(14)	2.022(12)
C(13)-C(14)	1.361(22)		
N(1)-Cu-N(2)	85.6(3)	C(13)-Cu-C(14)	39.6(6)
N(1)-Cu-C(13)	115.0(5)	N(1)-Cu-C(14)	154.6(5)
N(2)-Cu-C(14)	119.8(5)	N(2)-Cu-C(13)	159.2(5)
N(1)-Cu-C_t [b]	134.8(5)	N(2)-Cu-C_t [b]	139.5(5)

[a] Estimated standard deviations are in parentheses. [b] C_t represents the midpoint of the C(13)-C(14) bond.

Supplementary material. Tables of thermal parameters of non-hydrogen atoms, fractional coordinates of the hydrogen atoms, a complete list of bond distances and bond angles, and the structure factor amplitudes are available from the authors.

Discussion

The nature of coordination between the transition metal and olefin can be generally described by the Dewar–Chatt–Duncanson model [9] consisting of σ and π components. The σ component consists of σ-donation from the occupied bonding π-orbital of the olefin to a vacant σ-type metal orbital, while the π component represents π-back donation from a filled metal d_π orbital to the vacant antibonding $\pi^\star$ orbital of the olefin. An unusual structural feature of Cu^I–ethylene complexes is that the C–C bond distance of the coordinated ethylene is virtually the same as that for the free molecule. Thompson et al. implied that this was due to the predominance of σ-bonding from ethylene to the metal ion [3]. On the other hand, Munakata et al. [4] suggested importance of the π-back-donation for the Cu^I–ethylene bonding. They studied the formation constants of several copper(I)–olefin complexes ($[Cu(biL)(olefin)]^+$ (biL = bpy, phen and their derivatives; olefin = ethylene and its derivatives)) in solution and the chemical shifts of the ^1H NMR spectra of the olefin.

They found that the formation constants for the Cu^I–ethylene complexes in the reactions ($Cu(biL)^+ + C_2H_4 \rightleftarrows Cu(biL)(C_2H_4)^+$) increase with increasing pK_a of biL, and electron-donating substituents such as methyl on biL stabilize the ethylene complexes. In contrast, electron-withdrawing substituents such as Cl are destabilizing, and ^1H NMR peaks of the olefinic protons of $[Cu(biL)(C_2H_4)]^+$ move upfield as the pK_a value of biL increases. These facts indicate that the σ-donation from the biL to copper(I) is enhanced as the basicity of biL increases and the resulting electron-rich Cu^I enhances π-back-donation in the copper(I)–ethylene bonding. Since the π-back-donation from the d_π-orbital of metal to the antibonding $\pi^\star$ orbital of olefin is considered to cause lengthening of the C–C bond distance, the spectroscopic results seem in conflict with the crystal structure. This anomaly may, however, be resolved by applying the concept of a molecular Rydberg state [10] to the ethylene molecule bound to the metal ion. The Rydberg orbital of the ethylene molecule is a $3d_\pi$-orbital with its core at the center of the ethylene molecule. This orbital overlaps the $3d_\pi$ orbital of the Cu^I ion, and back-donation from the metal

$3d_\pi$ orbital to the Rydberg $3d_\pi$ orbital is then possible. The lengthening of the C–C bond distance cannot then occur owing to this back-donation, because this Rydberg $3d_\pi$ orbital is a non-bonding orbital for the C–C bond. In the Ni^0–ethylene complex [11] Ni^0 has a d^{10} configuration isoelectronic to Cu^I and a slightly longer C–C distance of 1.391(5) Å was reported. The difference between the Cu^I–ethylene and Ni^0–ethylene complexes may be explained by the difference in contribution of d_π(metal) → π^*(ethylene) and d_π(metal) → d_π(ethylene) to back-donation. The fraction of the d_π(metal) → d_π(ethylene) back-donation in the Cu^I–ethylene bond may be large compared with that in the Ni^0–ethylene bond. The higher-field shift of ^1H NMR peaks of the ethylene protons in the Ni^0–ethylene complexes (δ 1.9–3.5 ppm) [12] compared with those of the Cu^I–ethylene complexes (δ 4.7–5.3 ppm) [4] are consistent with the observed bond distances of ethylene, because d_π(metal) → π^* (ethylene) back-donation increases the electron density on the olefinic protons but the d_π(metal) → d_π(ethylene) back-donation does not increase.

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