7. Anal. Calcd for $C_{38}F_{10}H_{45}NO_2Pd$: C, 54.1; H, 5.4; N, 1.7. Found: C, 54.1; H, 5.7; N, 2.0. Mp: 270 °C dec. Λ_M: 92 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 795 s, 785 s (X-sensitive), 1590 vs (ν(C–C) + ν(C–O)), 1560 vs (ν(C–O) + ν(C–C)), 1400 s (CH_3 def), 460 m (ring def).[19]

8. Anal. Calcd for $C_{37}F_{10}H_{42}N_2OPd$: C, 53.0; H, 5.2; N, 3.4. Found: C, 52.8; H, 5.1; N, 3.6. Mp: 262 °C dec. Λ_M: 92 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 795 s, 780 s (X-sensitive), 1565 s, 820 s.

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}OH)(\mu\text{-dmpz})Pd(C_6F_5)_2]$ (9). A 20% aqueous solution of $(NBu_4)OH$ (0.139 mmol) was added to a methanol (7 cm^3) solution of 3,5-dimethylpyrazole (0.0695 mmol). After 10 min with constant stirring, $(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(C_6F_5)_2]$ (0.0695 mmol) was added and the solution was stirred at room temperature for 1 h. The solvent was then partially evaporated under vacuum, and water was added until precipitation of a white solid, which was separated by filtration and dried in air. Yield: 66%.

Anal. Calcd for $C_{61}F_{20}H_{82}N_{44}OPd_2$: C, 49.6; H, 5.5; N, 3.8. Found: C, 50.4; H, 5.8; N, 3.4. Mp: 216 °C dec. Λ_M: 179 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 785 sh, 780 s (X-sensitive), 3605 m (ν(OH)), 430 br (Pd–O).

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Supplementary Material Available: Listings of full crystal data, anisotropic thermal parameters, and fractional atomic coordinates for hydrogen atoms (3 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577, Japan, and Institute for Molecular Science, Myodaizi, Okazaki 444, Japan

Synthesis, Characterization, and Molecular Structures of Binary and Ternary Copper(I) Complexes with 1,5-Cyclooctadiene (cod): $[Cu(cod)_2]ClO_4$ and $[Cu(cod)(2,2'\text{-bipyridine})]PF_6$

Megumu Munakata,*,[†] Susumu Kitagawa,[†] Hisao Shimono,[†] and Hideki Masuda[‡]

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Binary and ternary copper(I) complexes with 1,5-cyclooctadiene (cod), $[Cu(cod)_2]ClO_4$ (**1**) and $[Cu(cod)(bpy)]PF_6$ (**2**) (bpy = 2,2'-bipyridine) have been prepared. The crystal structures have been determined by using single-crystal X-ray diffraction methods. Compound **1** crystallizes in the orthorhombic space group *Pnma*, with a = 17.434 (7) Å, b = 10.597 (4) Å, c = 8.718 (2) Å, Z = 4, and R = 0.073 for 913 reflections. Crystals of **2** are triclinic, space group $P\bar{1}$, with a = 9.774 (3) Å, b = 11.482 (2) Å, c = 8.959 (2) Å, α = 90.60 (2)°, β = 106.62 (2)°, γ = 83.09 (2)°, Z = 2, and R = 0.062 for 1542 reflections. The geometry about the Cu atom coordinated to the four olefinic moieties of the two cod molecules is quasi-tetrahedral in **1**. The Cu–C(olefin) distances of 2.27 Å (average) are significantly longer than those found for copper(I) olefin complexes, and the C=C bond distances of 1.33 Å (average) of the coordinated cod are almost the same that of free cod. On the basis of the C=C distance, the stretching frequencies of the C=C bonds and the ^{1}H NMR chemical shifts of the olefinic protons, the Cu–olefin bonds in **1** were concluded to be dominated by σ donation from the olefinic moiety to the copper. The geometry about the Cu atom coordinated to two nitrogen atoms of bpy and two olefinic moieties of the cod molecule is a very distorted tetrahedron in **2**. The Cu–C distances of 2.06 Å (average) of one olefinic moiety of the cod molecule are significantly shorter than those of the other olefinic moiety (2.44 Å (average)). In response to this, the C=C bond distance (1.36 (1) Å) of the former is longer than that (1.33 (1) Å) of the latter.

Introduction

Copper–olefin bonding is of both practical and theoretical interest in view of the catalytic activity of copper(I) toward olefin activation[1] and its role in biological systems.[2-4] Through the crystallographic study of mixed-ligand copper(I) complexes of ethylene,[2,4a] the important contribution of σ donation in copper(I)–olefin bonding has been inferred. In other words, the π back-donation is very weak.[2] This is supported by the fact that the upfield shifts of ^{1}H NMR signals of the ethylene protons of the copper(I) complexes with ethylene are small compared with those of Ni(0) and Pt(0) complexes with ethylene.[3] The copper(I) complexes with ethylene so far reported contain electron-donor nitrogen-based ligands. Such a ligand causes a trans influence,[5] which results in the enhancement of π back-donation from a dπ orbital of the metal to a π^* orbital of the olefin at the trans position.[3] It is of interest, therefore, to know the structure and the copper–olefin bonding of a Cu(I)–olefin complex without any strong electron-donor ligand, i.e. a Cu(I) complex having only olefin molecules.

No crystal structures of copper(I) complexes with only olefins have been reported so far, because the complexes are quite unstable under ambient conditions. The instability is increased by use of chelating dienes rather than monodentate olefins. A ternary copper(I) complex with 1,5-cyclooctadiene (cod) and chloride has been reported to have a centrosymmetric dimeric structure with the copper atoms quasi-tetrahedrally bonded to chlorine atoms and the two double bonds of the cod molecule.[6] Crystals of a copper(I) complex with two cod molecules, $[Cu(cod)_2]ClO_4$, have been prepared by electrolysis at a copper electrode of copper(II) perchlorate in the presence of cod in methanol.[7] The C=C stretching band at 1660 cm^{-1} in free cod is replaced by two bands at 1638 and 1595 cm^{-1} in the complex, suggesting nonequivalent coordination of the double bonds. We have synthesized suitable single crystals of the four-coordinate copper(I) complexes with

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[†] Kinki University.

[‡] Institute for Molecular Science.

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Table I. Crystal Data and Refinement Details for $[Cu(cod)_2]ClO_4$ (**1**) and $[Cu(cod)(bpy)]PF_6$ (**2**)

	1	**2**
formula	$CuClC_{16}H_{24}O_4$	$CuPF_6C_{18}N_2H_{20}$
fw	377.36	472.88
color	colorless	pale greenish yellow
cryst size, mm	0.2 × 0.2 × 0.2	0.10 × 0.10 × 0.05
cryst syst	orthorhombic	triclinic
space group	*Pnma*	$P\bar{1}$
a, Å	17.434 (7)	9.774 (3)
b, Å	10.597 (4)	11.482 (2)
c, Å	8.718 (2)	8.959 (2)
α, deg	90	90.60 (2)
β, deg	90	106.62 (2)
γ, deg	90	83.09 (2)
V, Å^3	1610.6	956.1 (4)
Z	4	2
temp, K	296	296
ρ_{calc}, g·cm^3	1.564	1.643
λ, Å	1.541 78 (Cu Kα)	0.710 69 (Mo Kα)
μ, cm^{-1}	35.76 (Cu Kα)	12.8 (Mo Kα)
$F(000)$	792.0	480.0
scan method	ω–2θ	ω–2θ
2θ range, deg	1.2 + 0.5 tan θ	0.8 + 0.35 tan θ
scan speed, deg·min^{-1}	8	4
tot. no. of reflcns	1311	5035
no. of reflcns used in refinement[a]	913	1542
R[b]	0.073	0.062
R_w[c]	0.085	0.067

[a] $|F_o| > 3\sigma(F_o)$. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w = \{\sum w(|F_o| - |F_c|)^2/w|F_o|^2\}^{1/2}$.

cod, $[Cu(cod)_2]ClO_4$, and $[Cu(cod)(bpy)]PF_6$ (bpy = 2,2′-bipyridine), determined the molecular structures of the complexes by means of X-ray crystallography, and examined the nature of the bonding between the Cu(I) and cod from the ^1H NMR, IR, and Raman spectra of the complexes.

Experimental Section

Material. $[Cu(CH_3CN)_4]PF_6$ was synthesized from copper(I) oxide according to a method described in the literature.[8] The obtained complex was checked by elementary analysis and an optical absorption method with the aid of the absorbance at 440 nm of a derived bis(2,2′-bipyridine)copper(I) complex in acetone (ϵ_{max} = 4800 M^{-1} cm^{-1}).[9] Copper wire, commercial grade, was washed with dilute HCl and water and dried before use. Copper(I) oxide, 2,2′-bipyridine, and 1,5-cyclooctadiene are commercially available. Acetone-d_6 (Merck, 99.8%) was used as a solvent for ^1H NMR measurement after drying over molecular sieves. High-purity nitrogen gas (99.9998%) was utilized.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and these should be handled with great caution.

Preparation of $[Cu(cod)_2]ClO_4$ (1). Copper(II) diperchlorate hexahydrates (0.15 mmol, 55.6 mg) were reduced with copper wire in a methanol (5 mL) solution of cod (15 mmol, 1.84 mL) for 30 min under ethylene to give the colorless complex **1** (yield 47%). The filtrate of the reaction solution was sealed in a glass tube and left at −10 °C. After 4 days, crystals of **1** suitable for X-ray diffraction studies were obtained.

Preparation of $[Cu(cod)(bpy)]PF_6$ (2). A solution of bpy (0.1 mmol, 15.6 mg) and cod (3.0 mmol, 0.36 mL) in ethanol (5 mL) was added to tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.1 mmol, 37.2 mg) under nitrogen and stirred for 30 min to give a pale greenish yellow solution. The filtrate of the reaction solution was sealed in a glass tube and left at 5 °C. After 4 days, greenish yellow crystals of **2** suitable for X-ray diffraction studies were obtained. Unfortunately, the biggest crystal of **2** selected for the diffraction study was of dimensions 0.10 × 0.10 × 0.05 mm, thus limitting the quality of the resulting data set.

^1H NMR Spectroscopy. ^1H NMR spectra were obtained in $(CD_3)_2CO$ at 200 MHz with a JEOL FX-200 NMR spectrometer, and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference.

Raman Spectroscopy. The Raman spectra were recorded on a JEOL S-1 laser Raman spectrometer using the 488.0-nm line of a Coherent Radiation 52G Ar$^+$ laser (70 mW at the sample position) as the excitation source. The slit width was 3.4–6.8 cm^{-1} in the region 2000–200 cm^{-1}. The observed frequencies were calibrated by the standard Raman shifts of liquid indene.[10]

Table II. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[Cu(cod)_2]ClO_4$[a]

atom	x	y	z	B_{eq}, Å^2
Cu	0.1081 (1)	0.2500	0.2238 (3)	3.15
Cl	0.1339 (3)	−0.2500	0.1513 (6)	4.97
C(1)	0.2324 (6)	0.3123 (13)	0.2071 (17)	4.76
C(2)	0.2356 (9)	0.3966 (17)	0.0691 (24)	7.49
C(3)	0.1768 (13)	0.3986 (17)	−0.0431 (21)	7.90
C(4)	0.1054 (7)	0.3136 (16)	−0.0246 (13)	5.04
C(5)	−0.0516 (8)	0.3206 (17)	0.3180 (24)	7.39
C(6)	0.0197 (7)	0.3927 (13)	0.3070 (16)	4.35
C(7)	0.0765 (8)	0.3923 (13)	0.4086 (16)	4.36
C(8)	0.0795 (14)	0.3232 (18)	0.5533 (17)	7.78
O(1)	0.1406 (13)	−0.1646 (89)	0.2848 (33)	15.95
O(2)	0.0908 (10)	−0.1537 (21)	0.0661 (34)	10.71
O(3)	0.2054 (9)	−0.2717 (58)	0.0964 (32)	11.35
O(4)	0.0873 (23)	−0.3562 (25)	0.1704 (78)	21.14

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

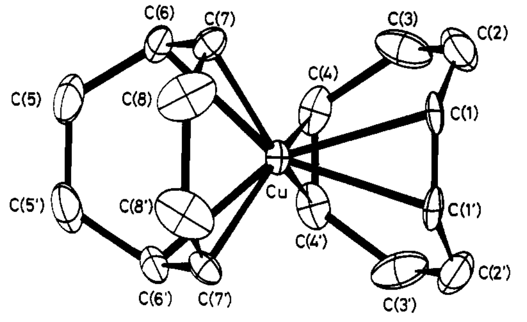

Figure 1. Molecular structure of $[Cu(cod)_2]ClO_4$. Atoms are represented by thermal ellipsoids at the 50% probability level.

X-ray Structure Analysis. Both crystals were coated with paraffin to avoid decomposition in the air. Diffraction data were measured on Rigaku AFC-6B and AFC-5R four-circle diffractometers for compounds **1** and **2**, respectively. Preliminary investigation revealed crystals **1** and **2** to be orthorhombic and triclinic, respectively. The unit cell parameters were determined by a least-squares fit of 25 accurately centered reflections with 2θ values from 41 to 55° for **1** and from 22 to 27° for **2**. Crystal data and details of measurements for compounds **1** and **2** are summerized in Table I. Three standard reflections for each crystal were monitored every 100 measurements, and the decay of their intensities was within 5%. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied as spherical for crsytal **1** and not applied for **2**, because the absorption coefficient for crystal **2** was very small (μ = 12.87 cm^{-1} for Mo Kα). For crystal **1**, the systematic absences ($0kl$ for $k + l = 2n + 1$, $hk0$ for $h = 2n + 1$, $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$) led to two possible space groups *Pnma* or $Pn2_1a$; the former was confirmed from the successful analysis. For crystal **2**, the intensity distribution suggested the centrosymmetric space group $P\bar{1}$. This was confirmed by the solution and refinement of the structure.

Both structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. In the structure analysis of **1**, a disorder of the perchlorate anion was observed on a crystallographic mirror-plane. Reliability factores are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where $w^{-1} = (\sigma^2(F_o) + (0.023F_o)^2)$ for **1** and $w^{-1} = (\sigma^2(F_o) + (0.020F_o)^2)$ for compound **2**. All hydrogen atoms were placed in calculated positions, but their parameters were not refined. The final R and R_w values were 0.073 and 0.085 for **1** and 0.062 and 0.067 for **2**. The final difference Fourier maps did not show any significant features. Atomic scattering factores and anomalous dispersion terms[11] were taken from ref 11. The calculations were performed on the FACOM M 780 computer at the Data Processing Center of Kyoto University by using

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Table III. Atomic Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms in [Cu(cod)(bpy)]PF$_6$[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Cu(1)	0.3165 (1)	0.2223 (1)	0.1344 (2)	5.48
P(1)	0.8565 (3)	0.2463 (3)	0.6231 (4)	4.8
F(1)	0.7217 (8)	0.1883 (6)	0.630 (1)	9.6
F(2)	0.8585 (8)	0.3162 (7)	0.7777 (8)	8.6
F(3)	0.859 (1)	0.177 (1)	0.481 (1)	18.0
F(4)	0.750 (1)	0.3517 (8)	0.540 (1)	16.8
F(5)	0.948 (1)	0.1441 (8)	0.726 (1)	16.5
F(6)	0.979 (1)	0.309 (1)	0.611 (1)	16.1
N(1)	0.3410 (8)	0.3224 (7)	−0.0373 (9)	4.1
N(2)	0.5099 (7)	0.1444 (7)	0.1307 (9)	3.6
C(1)	0.249 (1)	0.409 (1)	−0.120 (1)	5.0
C(2)	0.280 (1)	0.4757 (9)	−0.230 (1)	4.8
C(3)	0.415 (1)	0.4532 (9)	−0.253 (1)	4.6
C(4)	0.514 (1)	0.3640 (9)	−0.166 (1)	4.0
C(5)	0.473 (1)	0.2996 (8)	−0.059 (1)	3.1
C(6)	0.5686 (9)	0.1982 (7)	0.037 (1)	2.9
C(7)	0.703 (1)	0.1614 (8)	0.021 (1)	3.9
C(8)	0.782 (1)	0.0632 (9)	0.113 (1)	4.1
C(9)	0.724 (1)	0.0077 (8)	0.209 (1)	4.0
C(10)	0.588 (1)	0.050 (1)	0.213 (1)	4.9
C(11)	0.192 (1)	0.1175 (8)	0.222 (1)	3.5
C(12)	0.103 (1)	0.203 (1)	0.125 (1)	4.0
C(13)	0.033 (1)	0.316 (1)	0.170 (1)	4.9
C(14)	0.120 (1)	0.381 (1)	0.302 (2)	6.3
C(15)	0.277 (1)	0.3761 (8)	0.317 (1)	4.2
C(16)	0.378 (1)	0.2929 (9)	0.395 (1)	4.2
C(17)	0.361 (1)	0.182 (1)	0.478 (1)	6.0
C(18)	0.234 (1)	0.119 (1)	0.399 (1)	5.1

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Distances (Å) and Angles (deg) for [Cu(cod)$_2$]ClO$_4$[a]

	Bond Distances		
Cu–C(1)	2.270 (11)	Cu–C(4)	2.268 (12)
Cu–C(6)	2.278 (13)	Cu–C(7)	2.274 (14)
C(1)–C(2)	1.500 (25)	C(2)–C(3)	1.417 (28)
C(3)–C(4)	1.545 (25)	C(5)–C(6)	1.462 (20)
C(4)–C(4′)	1.348 (24)	C(5)–C(5′)	1.496 (25)
C(6)–C(7)	1.329 (19)	C(7)–C(8)	1.460 (21)
C(1)–C(1′)	1.320 (19)	C(8)–C(8′)	1.551 (27)
	Bond Angles		
C(1)–Cu–C(4)	82.7 (5)	C(1)–Cu–C(6)	118.2 (5)
C(1)–Cu–C(7)	94.8 (5)	C(4)–Cu–C(6)	93.3 (5)
C(4)–Cu–C(7)	118.3 (5)	C(6)–Cu–C(7)	33.9 (5)
C(1)–Cu–C(1′)	33.8 (5)	C(1)–Cu–C(4′)	92.6 (5)
C(1)–Cu–C(6′)	149.3 (5)	C(1)–Cu–C(7′)	118.0 (5)
C(4)–Cu–C(4′)	34.6 (6)	C(4)–Cu–C(6′)	119.2 (5)
C(4)–Cu–C(7′)	150.2 (5)	C(6)–Cu–C(6′)	83.2 (5)
C(6)–Cu–C(7′)	92.9 (5)	C(7)–Cu–C(7′)	83.1 (5)
C(2)–C(3)–C(4)	120.1 (15)	C(1)–C(2)–C(3)	122.4 (15)
C(5)–C(6)–C(7)	126.0 (14)	C(6)–C(7)–C(8)	127.2 (15)

[a] The primed and unprimed atoms are related by a mirror plane.

Table V. Selected Bond Distances (Å) and Angles (deg) for [Cu(cod)(bpy)]PF$_6$

	Bond Distances		
Cu–N(1)	2.015 (7)	Cu–N(2)	2.000 (7)
Cu–C(11)	2.113 (8)	Cu–C(12)	2.105 (9)
Cu–C(15)	2.47 (1)	Cu–C(16)	2.40 (1)
C(11)–C(18)	1.52 (1)	C(11)–C(12)	1.36 (1)
C(13)–C(14)	1.49 (1)	C(12)–C(13)	1.50 (1)
C(15)–C(16)	1.33 (1)	C(14)–C(15)	1.49 (1)
C(17)–C(18)	1.51 (1)	C(16)–C(17)	1.53 (1)
	Bond Angles		
C(11)–Cu–C(12)	37.6 (3)	C(11)–Cu–C(15)	88.9 (3)
C(11)–Cu–C(16)	83.0 (4)	C(12)–Cu–C(15)	80.9 (4)
C(12)–Cu–C(16)	94.9 (4)	C(15)–Cu–C(16)	31.7 (3)
Cu–C(11)–C(12)	70.9 (5)	Cu–C(11)–C(18)	110.8 (6)
C(12)–C(11)–C(18)	125.2 (9)	Cu–C(12)–C(11)	71.5 (5)
Cu–C(12)–C(13)	108.7 (7)	N(1)–Cu–C(11)	150.4 (4)
N(1)–Cu–N(2)	82.4 (3)	N(1)–Cu–C(15)	100.0 (3)
N(1)–Cu–C(12)	115.8 (4)	N(2)–Cu–C(11)	115.6 (3)
N(1)–Cu–C(16)	118.7 (3)	N(2)–Cu–C(15)	124.6 (3)
N(2)–Cu–C(12)	147.3 (4)	N(2)–Cu–C(16)	99.4 (3)

the program system KPPXRAY[12] for **1** and on the VAX computer by using the program system TEXAN[13] for **2**.

The final atomic parameters for non-hydrogen atoms for **1** and **2** are given in Tables II and III, respectively, and the selected bond distances and angles are listed in Tables IV and V, respectively.

Results

[Cu(cod)$_2$]ClO$_4$. The crystal structure shown in Figure 1 is the first binary Cu(I) complex with only olefin molecules. The structure consists of a four-coordinate Cu(I) cation, which lies on a crystallographic mirror plane, and a ClO$_4^-$ anion. The perchlorate anion is not coordinated to the copper, the shortest Cu···O(ClO$_4$) distance being 4.22 Å. The geometry about the Cu atom coordinated to four olefinic moieties of two cod molecules is a quasi-tetrahedral structure; this structure is analogous to those found in the isoelectronic metal compounds [Ni(cod)$_2$],[14] [Ag(cod)$_2$]BF$_4$,[15] and [Pt(cod)$_2$].[16] The geometry of the cod groups coordinated to the central copper atom is also consistent with those of the isoelectronic metal compounds.[14-16] The eight olefinic carbon atoms of [Cu(cod)$_2$]$^+$ are symmetrically bound to the copper atom within experimental error and the four C=C bond distances are almost the same, whereas the eight olefinic carbon atoms of [Pt(cod)$_2$] are not symmetrically bound to the platinum atom.[16]

The Cu–C(olefin) distances of 2.27 Å (average) for [Cu(cod)$_2$]ClO$_4$ are significantly long compared with the 2.14-Å (average) distance for the binuclear Cu(I) complex with cod and Cl, [Cu$_2$(cod)$_2$Cl$_2$],[6] and those (1.96–2.03 Å) for the ternary Cu(I) complexes with olefins and nitrogenous ligands.[2,4]

The metal–C(olefin) distances have been found to be longer in the binary nickel(0) complex [Ni(cod)$_2$] (2.12 (2) Å)[14] than in the ternary complexes [Ni(cod)(bpy)] (2.052 (5) Å)[17a] and [Ni(C$_2$H$_4$){(*o*-CH$_3$C$_6$H$_4$O)$_3$P}$_2$] (2.02 (2) Å).[17b] Thus, the binary d^{10} metal complexes having only olefin molecules show longer metal–olefin bonds. The d^{10} metal–olefin bonds are shorter in group VIII metals than in the group IB metals: [Ni(cod)$_2$] (2.12 (2) Å)[14] < [Pt(cod)$_2$] (2.21 (1) Å)[16] < [Cu(cod)$_2$]ClO$_4$ (2.27 (1) Å) < [Ag(cod)$_2$]BF$_4$ (2.50 (2) Å).[15]

The C=C distances of 1.33 (2) Å (average) found in [Cu(cod)$_2$](ClO$_4$) are essentially the same as that for the free cod molecule (1.34 Å (average)),[18] and are comparable to the C=C distances of 1.34 (2) Å for [Ag(cod)$_2$]BF$_4$.[15] The C=C distances of group IB metal complexes with cod, [Cu(cod)$_2$]ClO$_4$ and [Ag(cod)$_2$]BF$_4$, are significantly shorter than those of group VIII metal complexes with cod, [Ni(cod)$_2$] (1.39 (1) Å (average))[14] and [Pt(cod)$_2$] (1.40 (1) Å (average)).[16].

The C=C stretching frequencies of [Cu(cod)$_2$]ClO$_4$ and free cod have been observed[19] at 1598 and 1667 cm^{-1}. The coordination of the cod molecules to the copper(I) atom results in only a small decrease (69 cm^{-1}) of the C=C stretching frequency. This decrease is comparable to those for [Ag(cod)$_2$]BF$_4$ (64 cm^{-1}) and Ag(C$_2$H$_4$)$^+$,[20] whereas it is smaller than those for [Pt(cod)$_2$] (202 cm^{-1}).[21]

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Table VI. ^{1}H NMR Chemical Shifts, Stretching Frequencies, and C=C and Metal—Carbon Distances of the Olefinic Moieties of the cod Ligand in the Metal Complexes with cod

	distance, Å		$\delta(^{1}H)$ of olefinic protons, ppm	ν(C=C), cm^{-1}
	C=C(av)	M—C(av)		
cod^{a}	1.34		5.51,^{b} 6.8 (−90 °C)^{b}	1667,^{b} 1280^{b}
$[Ag(cod)_2]PF_4$^{c}	1.34 (2)	2.50 (1)	5.68^{b}	1603
$[Cu(cod)_2]ClO_4$^{b}	1.33 (2)	2.27 (1)	5.78	1598,^{d} 1267^{d}
$[Ni(cod)_2]$^{e}	1.39 (1)	2.12 (2)	4.3^{a}	
$[Pt(cod)_2]$^{f}	1.40 (1)	2.21 (1)	4.2^{g}	1475,^{g} 1238^{g}
$[Cu(cod)(bpy)]PF_6$^{b}	1.37 (2) 1.32 (2)	2.09 (1) 2.44 (1)	5.82	1603, 1491
$[Cu_2(cod)_2Cl_2]$^{h}	1.40	2.19		
$[Ni(cod)(bpy)]$^{i}	1.38 (1)	2.051 (6)	3.9	
$[Pd_2(cod)_2Cl_2]$^{j}	1.35 (1)	2.17 (1)		
$[Pd(cod)Cl_2]$^{k}	1.39 (1)	2.21 (1)		1515
$[Pt(cod)(Cp)(CH_3)]$^{l}	1.38 (1)	2.23 (1)		
$[Pt(cod)Cl_2]$^{m}	1.38 (1)	2.17		

^{a}References 17a, 18. ^{b}This work. ^{c}Reference 15. ^{d}Reference 19. ^{e}Reference 14. ^{f}Reference 16. ^{g}Reference 21. ^{h}Reference 6. ^{i}Reference 17a. ^{j}Reference 26. ^{k}Reference 25. ^{l}Reference 23. ^{m}Reference 24.

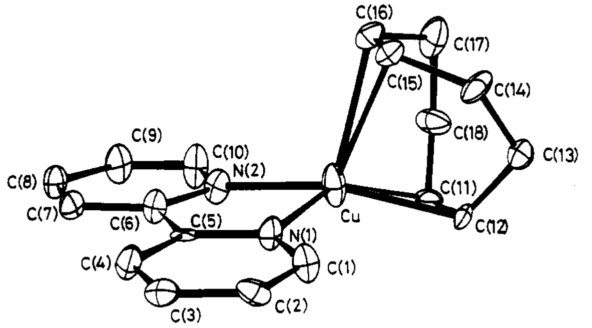

Figure 2. Molecular structure of $[Cu(cod)(bpy)]PF_6$. Atoms are represented by thermal ellipsoids at the 50% probability.

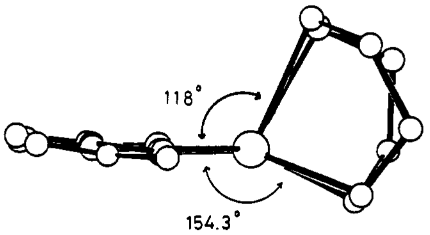

Figure 3. Angles between the plane defined by Cu, N(1), and N(2), and the axial or equatorial plane of the cod in $[Cu(cod)(bpy)]PF_6$.

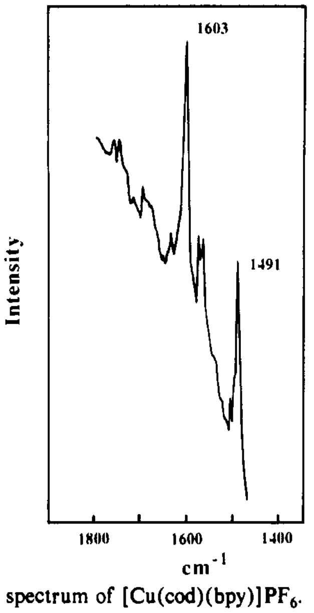

Figure 4. Raman spectrum of $[Cu(cod)(bpy)]PF_6$.

^{1}H NMR resonances of olefinic protons of free cod and $[Cu(cod)_2]ClO_4$ in acetone-d_6 were observed at 5.52 and 5.78 ppm, respectively. The ^{1}H chemical shifts of the olefinic protons, metal-olefinic carbon and C=C distances in the metal complexes with cod are summarized in Table VI. The resonances of olefinic protons of free cod shift downfield in $[Cu(cod)_2]ClO_4$ and $[Ag(cod)_2]BF_4$, whereas they shift upfield in $[Ni(cod)_2]$[20] and $[Pt(cod)_2]$.[21]

$[Cu(cod)(bpy)]PF_6$. The molecular structure is depicted in Figure 2. The structure consists of a four-coordinate copper(I) cation and a PF_6^- anion. The hexafluorophosphate anion is not coordinated to the copper, the shortest Cu···F(PF_6) distance being 4.51 (1) Å. The geometry about the Cu atom, which is coordinated to two nitrogen atoms of bpy and two olefinic moieties of the cod molecule, is a very distorted tetrahedron. The angle between the planes defined by Cu, C(11), and C(12), and Cu, N(1), and N(2) is ca. 154° and the angle between the planes defined by Cu, N(1), and N(2) and Cu, C(15), and C(16) is ca. 118° (Figure 3). The Cu–N distances of 2.01 Å (average) are longer than those of 1.94 Å (average) for $[Ni(cod)(bpy)]$[17a] and fall in the range observed for three-coordinate copper(I) complexes with ethylene $[Cu(C_2H_4)(biL)]^+$ (biL = bpy, 1,10-phenanthroline(phen) and 2,2′-bipyridylamine).[2d,4a] On the other hand they are shorter than those of four-coordinate copper(I) complexes with bpy, phen, and their derivatives (2.02–2.07 Å).[22] The Cu–C distances of 2.113 (8) and 2.105 (9) Å for the equatorially coordinated olefinic moiety (C(11)=C(12)) are slightly longer than those (1.96–2.03 Å)[2,4] reported for ternary copper (I) complexes, and the distances of 2.47 (1) and 2.40 (1) Å for the axially coordinated olefinic moiety (C(15)=C(16)) are extremely long, indicating a weak Cu—C bond. The C=C distance of 1.33 (1) Å for the axial olefinic moiety is essentially the same as the value for the free cod molecule (1.34 Å (average)), whereas the C=C distance of 1.36 (1) Å for the equatorial olefinic moiety is long and within the range of 1.35–1.38 Å reported for d^8 metal ternary complexes with cod.[23-27]

The Raman spectrum of $[Cu(cod)(bpy)]PF_6$ was measured (Figure 4). The cod molecule exhibits two strong bands at 1603 and 1491 cm^{-1}, which can be assigned to the axial and equatorial

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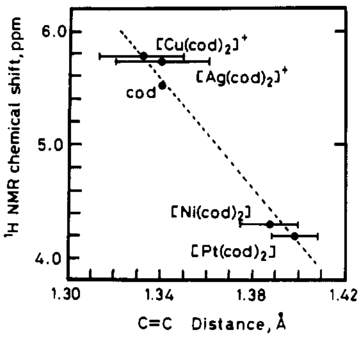

Figure 5. Correlation between the ^{1}H NMR chemical shifts of the olefinic protons and the C═C bond distances of metal-free cod[18] and the metal complexes.[14-17a]

C═C stretching frequencies, respectively.

Discussion

The most striking feature of the binary complex [Cu(cod)$_2$]ClO$_4$ is the significantly long Cu–C(olefin) distances of 2.27 Å, indicative of a weak copper–cod bond. The π back-donation from the occupied dπ orbitals of a metal to the unoccupied π^* antibonding orbital of an olefin molecule causes the elongation of the C═C distance of the olefin. No elongation of the C═C distance in [Cu(cod)$_2$]ClO$_4$ indicates that the contribution of the π back-donation to the copper–cod bonds is extremely small, and σ donation from the occupied π orbital of cod molecule to the vacant σ type orbital of the metals is predominant in the copper–cod bonds.

In a metal olefin complex in which the π back-donation contributes to the metal–olefin bond, the ^{1}H NMR signals of the olefinic protons shift upfield due to increased shielding of the protons caused by the π back-donation. For example, the ^{1}H NMR resonances of ethylene (5.44 ppm) slightly move upfield upon coordination to copper (5.3–4.7 ppm)[3] contrasted with a significantly greater upfield shift upon coordination to platinum (2.6–4.7 ppm),[28] nickel (1.9–2.0 ppm),[28b,29] niobium (0.6–1.3 ppm),[30] and rhodium (1.4–1.9 ppm).[31] A small upfield shift of the resonances of olefinic protons has been also observed for copper(I) complexes with 2-vinylpyridine[4c] and styrene.[4b] The silver(I) ethylene complex, on the contrary, exhibits a downfield shift (5.7 ppm).[28b] The ^{1}H NMR chemical shifts of the olefinic protons of cod and the metal complexes correlate with the C═C bond distance as shown in Figure 5: The ^{1}H NMR resonances of the olefinic protons shift upfield with elongation of the C═C bond distances. The downfield shift in [Cu(cod)$_2$]ClO$_4$ indicates again that the contribution of π back-donation is negligibly small. The relatively small decrease (69 cm^{-1}) of the C═C stretching frequency of the coordinated cod molecule of [Cu(cod)$_2$]ClO$_4$ from the free cod value suggests that the Cu–cod bonding is similar to the Ag–olefin bondings, which are dominated by σ donation.[20] On the other hand, the large decrease of the C═C stretching frequency of 163–202 cm^{-1} for Pt(0) complexes with cod[21,32] have been observed because of π back-bonding interaction from the metal ion to the olefin.

All of the results obtained from the C═C bond distances, the ^{1}H NMR chemical shifts, and the C═C stretching frequencies of the olefinic moieties in [Cu(cod)$_2$]ClO$_4$ clearly demonstrate that the copper–olefin bond is dominated by σ donation and the π back-bond between Cu and olefin is extremely weak.

The Cu–C distances of 2.45 Å (average) for the axial olefinic moiety of the ternary complex [Cu(cod)(bpy)]PF$_6$ are significantly longer than those of 2.11 Å (average) for the equatorial olefinic moiety. In response to this, the equatorial C(11)═C(12) distance of 1.36 (1) Å is longer than the axial C(15)═C(16) distance of 1.33 (1) Å, which is essentially the same as that of free cod molecule. The C═C stretching frequencies of the equatorial olefinic moiety are lower than that of the axial olefinic moiety. This reflects well π back-donation from the copper to the equatorial olefinic moiety. On the other hand, the two C═C distances of the cod molecule are essentially the same in the isoelectronic metal compound [Ni(cod)(bpy)].[17a] The complex [Cu(cod)(bpy)]PF$_6$ exhibits a single ^{1}H NMR signal (5.82 ppm) of the olefinic protons in the acetone solution at 23 °C, showing the rapid chemical exchange between both olefinic moieties in solution.

In conclusion, the Cu atom of the binary copper(I) complex with cod, [Cu(cod)$_2$]ClO$_4$, is tetrahedrally coordinated to four olefinic moieties of the two cod molecules. The copper–olefin bonds are dominated by σ donation from the olefinic moiety to the copper. The geometry about the Cu atom coordinated to two nitrogen atoms by bpy and two olefinic moieties of the cod molecule in the ternary copper(I) complex [Cu(cod)(bpy)]PF$_6$ is a very distorted tetrahedral. The copper–carbon distances are normal for one olefinic moiety of the cod molecule, whereas those are unusually long for the other olefinic moiety, indicating a weak copper–olefin bond.

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Supplementary Material Available: For [Cu(cod)$_2$]ClO$_4$ and [Cu(cod)(bpy)]PF$_6$, respectively, tables of atomic parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond distances, and valence angles (20 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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