Synthesis and Structural Study of (2,2′-Bipyridine)perchlorato(styrene)-copper(I)†

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The reduction of $Cu(ClO_4)_2 \cdot 6H_2O$ with copper wire in the presence of styrene and 2,2′-bipyridine (bipy) gave the complex $[Cu^I(bipy)(CH_2{=}CHPh)(ClO_4)]$ in methanol. The complex has been characterized by spectroscopic and *X*-ray diffraction studies. Crystals of the complex are monoclinic, space group $P2_1/n$, with a = 12.154(3), b = 14.796(4), c = 10.361(2) Å, β = 111.04(2)°, and Z = 4. The geometry about the copper(I) atom is trigonal pyramidal, involving two nitrogen atoms of bipy and two carbon atoms of the olefinic moiety of styrene at equatorial positions in an approximately planar fashion and weak co-ordination to an oxygen atom of the perchlorate anion at the axial position. The olefinic C=C bond distance of the co-ordinated styrene molecule, 1.358(10) Å, is slightly longer than those reported for other free olefin molecules. This slight lengthening is reflected in the ^1H n.m.r spectrum of the olefinic protons and the C=C stretching frequency of the co-ordinated styrene in the Raman spectrum and suggests the importance of d_π(metal)$\rightarrow\pi^*$(styrene) back donation in the copper(I)–olefin bonding.

The syntheses and structural characterization of copper(I) complexes with olefins have been of great interest in connection with the proposed role of copper at the receptor site of the plant hormone ethylene.[1–4] These complexes are generally unstable. If copper is indeed the binding site for ethylene in plants, it is expected that Cu^I will form stable complexes with all of the biologically active olefins. Our interest in this subject arises from the nature of co-ordination between the copper atom and olefins. Recently, on the basis of structural studies of copper(I) ethylene complexes, Thompson and co-workers[1,2] suggested that the nature of the copper(I)–ethylene bonding is dominated by σ donation from the ethylene molecule to the Cu^I and the π back donation from the Cu^I to the ethylene π^* orbital is negligible. On the other hand, π back donation has been demonstrated by studies on the formation constants and ^1H n.m.r. spectra of several copper(I)–ethylene complexes, although it is not dominant.[3]

Here, we present the synthesis, spectroscopy, and structure of a trigonal copper(I) complex with styrene, $[Cu(bipy)(CH_2{=}CHPh)(ClO_4)]$ (bipy = 2,2′-bipyridine), and discuss the nature of the copper–styrene bonding.

Experimental

Preparation.—Copper diperchlorate hexahydrate (46.3 mg, 0.125 mmol) in methanol (2.5 cm³) was reduced with copper wire to copper(I) under ethylene ($Cu^{2+} + Cu \longrightarrow 2Cu^+$). To the reaction solution 2,2′-bipyridine (39 mg, 0.25 mmol) and styrene (0.29 cm³, 2.5 mmol) were added to form the pale yellow complex $[Cu(bipy)(CH_2{=}CHPh)(ClO_4)]$ (Found: C, 51.1; H, 3.75; N, 4,65. Calc. for $C_{18}H_{16}ClCuN_2O_4$: C, 51.05; H, 3.80; N, 6.60%). After several days, crystals were obtained from this solution in a sealed glass tube at room temperature.

Spectroscopy.—Proton n.m.r. spectra were obtained in CD_3OD at 200 MHz with a JEOL FX-200 NMR spectrometer and chemical shifts are given in p.p.m. relative to tetramethylsilane as internal reference. Raman spectra were recorded on a JEOL S-1 laser Raman spectrometer by 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 2 000—200 cm^{-1}. The observed frequencies were calibrated by the standard Raman shifts of liquid indene.[5]

Crystallography.—A yellowish prism-like crystal with dimensions of *ca.* 0.3 × 0.3 × 0.3 mm was used for the determination and the collection of intensity data at 296 K. The cell dimensions and the diffraction intensities were measured on a Rigaku AFC-6B diffractometer by using graphite-monochromated Cu-K_α radiation ($\bar{\lambda}$ = 1.541 78 Å).

Crystal data. $C_{18}H_{16}ClCuN_2O_4$, M = 423.32, space group $P2_1/n$ (monoclinic), a = 12.154(3), b = 14.796(4), c = 10.361(2) Å, β = 111.04(2)°, Z = 4, D_c = 1.617 g cm^{-3}, μ = 34.26 cm^{-1}, $F(000)$ = 864.

All independent reflections within the range $2\theta < 120°$ were collected by the use of the ω–2θ scan mode and a scanning rate of 8° min^{-1}. Three reflections were monitored every 56 reflections. There was no significant variation of the intensities during data collection. The intensity data were converted to F_o data in the usual manner. No absorption correction was applied. The standard deviations, $\sigma(F_o)$, were estimated by counting statistics. A total of 2 327 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the determination of the crystal structure.

Structure determination. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares refinement. Several cycles of refinement including anisotropic thermal parameters were carried out with the weighting scheme $w = 1/\sigma^2(F_o)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 6. The hydrogen atoms were included and refined as isotropic in the last cycle; their positions were obtained from the Fourier difference synthesis. The final R and R' values were 0.048 and 0.052, respectively. The final Fourier difference map showed no significant features. All calculations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY.[7]

The final atomic parameters for the non-hydrogen atoms are listed in Table 1.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Final atomic co-ordinates for [Cu(bipy)(CH_2=CHPh)(ClO_4)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	0.206 3(1)	0.064 7(0)	0.744 7(1)	C(13)	−0.087 8(4)	−0.094 2(4)	0.743 2(6)
Cl	0.298 8(1)	−0.078 9(1)	0.043 9(1)	C(14)	−0.089 1(4)	−0.160 1(4)	0.649 9(6)
N(11)	0.073 8(3)	−0.021 8(3)	0.708 8(4)	C(15)	−0.009 1(4)	−0.155 4(3)	0.584 5(6)
N(18)	0.239 4(3)	−0.007 6(3)	0.601 6(4)	C(16)	0.072 0(4)	−0.085 4(3)	0.615 4(5)
C(1)	0.116 9(4)	0.228 5(3)	0.834 3(5)	C(17)	0.162 8(4)	−0.075 8(3)	0.551 7(5)
C(2)	0.036 9(5)	0.215 4(4)	0.901 2(6)	C(19)	0.324 8(4)	0.004 7(4)	0.549 8(6)
C(3)	−0.061 4(5)	0.271 4(5)	0.871 9(7)	C(20)	0.337 0(5)	−0.048 4(4)	0.448 7(6)
C(4)	−0.080 9(5)	0.339 7(4)	0.776 1(7)	C(21)	0.259 0(5)	−0.117 0(4)	0.397 9(6)
C(5)	−0.002 8(5)	0.352 7(4)	0.710 4(6)	C(22)	0.170 9(4)	−0.130 8(4)	0.448 2(5)
C(6)	0.095 2(4)	0.298 6(3)	0.738 3(5)	O(1)	0.219 5(4)	−0.023 0(3)	1.079 6(5)
C(7)	0.223 0(5)	0.171 6(3)	0.870 7(6)	O(2)	0.396 5(4)	−0.103 9(4)	1.164 2(5)
C(8)	0.306 6(5)	0.173 2(4)	0.812 1(7)	O(3)	0.239 5(4)	−0.158 9(3)	0.979 2(5)
C(12)	−0.005 7(4)	−0.026 2(3)	0.770 4(6)	O(4)	0.340 1(4)	−0.031 6(3)	0.950 0(4)

Table 2. Selected bond distances (Å) and angles (°) for [Cu(bipy)-(CH_2=CHPh)(ClO_4)] along with their e.s.d.s in parentheses

Cu–N(11)	1.985(4)	Cu–N(18)	1.983(5)
Cu–C(7)	2.014(5)	Cu–C(8)	1.985(6)
Cu–O(4)	2.591(4)	Cu(7)–C(1)	1.471(7)
C(7)–C(8)	1.358(10)		
N(11)–Cu–N(12)	83.2(2)	N(11)–Cu–C(7)	120.9(2)
N(11)–Cu–C(8)	160.3(2)	N(18)–Cu–C(7)	155.2(2)
N(18)–Cu–C(8)	115.8(2)	C(7)–Cu–C(8)	39.7(2)
Cu–C(7)–C(8)	69.0(4)	Cu–C(7)–C(1)	114.1(3)
C(8)–C(7)–C(1)	127.1(5)	O(4)–Cu–N(18)	94.7(2)
O(4)–Cu–N(11)	91.6(2)	O(4)–Cu–C(8)	91.7(2)
O(4)–Cu–C(7)	90.7(2)		

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Results

Crystal Structure.—The molecular structure of the complex together with the atomic numbering is shown in Figure 1. The co-ordination about the Cu^I, involving two nitrogen atoms of bipy and two olefinic carbon atoms of styrene at the equatorial positions and a weakly co-ordinated oxygen atom of perchlorate anion (semi-co-ordination) at the axial position, is trigonal pyramidal. The copper and two nitrogen and two carbon atoms are planar to within 0.08 Å. The dihedral angle between the planes defined by the copper and two nitrogen atoms of the bipy molecule and by the copper and two carbon atoms of styrene is 5.44°.

Selected bond distances and angles are presented in Table 2. The Cu–N bond distances, av. 1.984(4) Å, are in the range generally found for copper(I) complexes with nitrogen-containing ligands (1.93—2.16 Å).[1,2,4,8] The Cu–O(ClO_4) distance, 2.591(4) Å, is slightly longer than the sum of ionic radii for Cu^I (0.96 Å) and O^-(1.40 Å),[9] but is in agreement with the distance of 2.6 Å at which ClO_4^- is weakly co-ordinated (semi-co-ordination) in copper(II) complexes.[10] The agreement suggests that the present Cu^I–$OClO_3$ distance represents semi-co-ordination, because the ionic radius of Cu^{II} (0.73 Å)[9] is smaller than that of Cu^I. The two Cu–C bond distances also fall in the range (1.93—2.07 Å) observed previously.[1,2,4] These distances are non-symmetric, the Cu^I being significantly closer to the terminal carbon [1.985(6) Å] than to the inner carbon [2.014(5) Å]. The difference in the two Cu–C(olefin) distances is consistent with the chemical shifts in the ^1H n.m.r. spectrum of the complex as described below. The C–C double-bond distance of the co-ordinated styrene, 1.358(10) Å, is slightly longer than those reported for other free olefin molecules (1.355 ± 0.005 Å),[11] although no direct comparison can be made owing to the unknown crystal structure of free styrene.

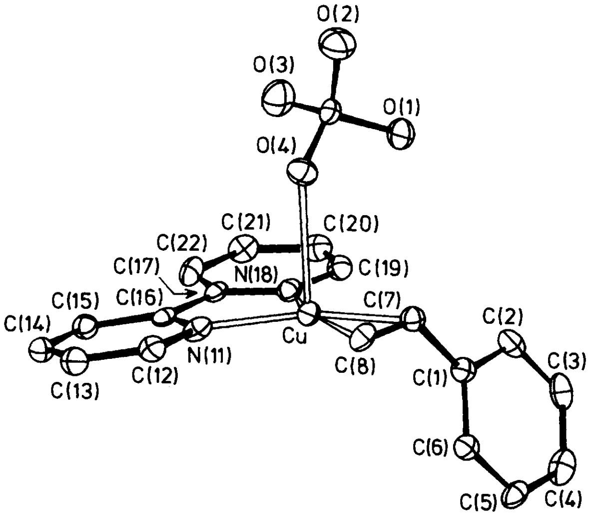


Figure 1. Molecular structure of [Cu(bipy)(CH_2=CHPh)(ClO_4)]. Atoms are represented by thermal ellipsoids at the 20% probability level

The co-ordination of styrene to the copper ion is accompanied by a twisting (4.72°) between the styrene phenyl ring and vinyl group and by a bending back (12.6°) of the phenyl group from the ethylenic plane as defined by the angle between the planes, Cu,C(7),C(8) and C(7),C(8),C(1). The two planar bipy moieties related by a centre of symmetry are packed in a parallel fashion (3.44 Å), and each is also packed with the styrene phenyl ring of the other [Cu(bipy)(CH_2=CHPh)]$^+$ cation (3.37 Å), as shown in Figure 2.

^1H *N.M.R. Spectrum.*—The ^1H n.m.r. chemical shifts for the olefinic protons of [Cu(bipy)(CH_2=CHPh)(ClO_4)] in CD_3OD at −55 °C are listed in Table 3, and compared with those of free styrene. All olefinic proton resonances of styrene appeared to shift upfield on co-ordination, although there were differences in their magnitudes. The difference is reflected in the *X*-ray structure; olefinic proton resonances move upfield together with shortening of the Cu–C bond distance. This result correlates also with the height of the frontier π-electron density; the terminal carbon with higher frontier π-electron density approaches copper(I) closer than the inner carbon with lower density.[12]

The ^1H n.m.r. data suggest that the bonding interaction between copper and the vinyl group of styrene is due to the π back donation from copper, because the upfield shift of the olefinic proton resonances on co-ordination reflects the shielding of the olefinic proton nuclei due to π back donation from metal to olefin.[13]

Raman Spectrum.—The Raman spectrum of the complex (solid) is shown in Figure 3. Although it is difficult to assign it completely, the C=C stretching frequency of the co-ordinated vinyl group has been tentatively assigned in comparison with spectra of analogous complexes[14] and the free ligands.[15] The observed value is typical of olefin complexes in general.[16] Sytrene exhibits a C=C stretching frequency at 1 640 cm^{-1}, whereas the [Cu(bipy)(CH$_2$=CHPh)(ClO$_4$)] complex shows this stretching frequency at 1 530 cm^{-1}. The C=C stretching frequency of styrene thus decreases by 110 cm^{-1} on co-ordination to Cu^I; this suggests a decrease in double-bond character (the C–C frequency in alkenes is at *ca.* 1 600 cm^{-1}, in alkanes at *ca.* 990 cm^{-1}).[16]

Two vibrations at 417 and 522 cm^{-1} appeared in the region from 600 and 350 cm^{-1} where metal–carbon stretching frequencies have been identified for complexes studied earlier,[17] and may be assigned as the two Cu–C stretching frequencies.

Discussion

Copper(I) generally prefers a four-co-ordinate geometry, and its complexes are almost in a tetrahedral arrangement. Previously the crystal structure of [Cu^I(en)(CO)(PhBPh$_3$)] had been reported as completing the distorted trigonal-pyramidal four-co-ordination around copper; the two nitrogen atoms of en (ethylenediamine) and the carbon atom of carbon monoxide are arranged in a distorted trigonal geometry, which interacts with one of the C=C bonds of the BPh$_4^-$ anion.[18] The bond distances between Cu and the carbon atoms of the phenyl ring, 2.919(5) and 2.706(4) Å, however, are too long to consider as co-ordination bonds, rather as electrostatic interactions. Thus

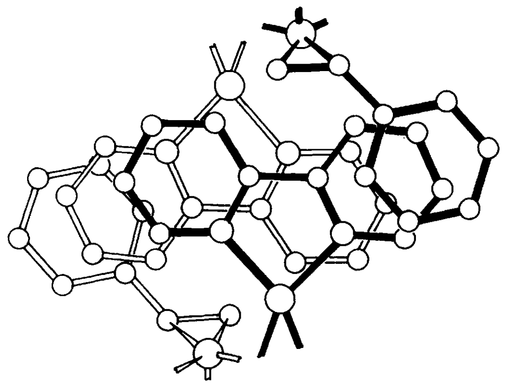
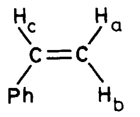


Figure 2. View showing the stacking interactions between bipy ligands and between bipy and the styrene phenyl ring

Table 3. Proton n.m.r. chemical shifts of olefinic protons for [Cu(bipy)-(CH$_2$=CHPh)(ClO$_4$)] and styrene in CD$_3$OD at −55 °C



	H$_a$	H$_b$	H$_c$
[Cu(bipy)(CH$_2$=CHPh)(ClO$_4$)]	5.03 (d)	5.63 (d)	6.68 (q)
Styrene	5.22 (d)	5.79 (d)	6.71 (q)
$\Delta(\delta_{complex} - \delta_{free})$*	−0.19	−0.16	−0.03

* A negative sign indicates an upfield shift from free styrene.

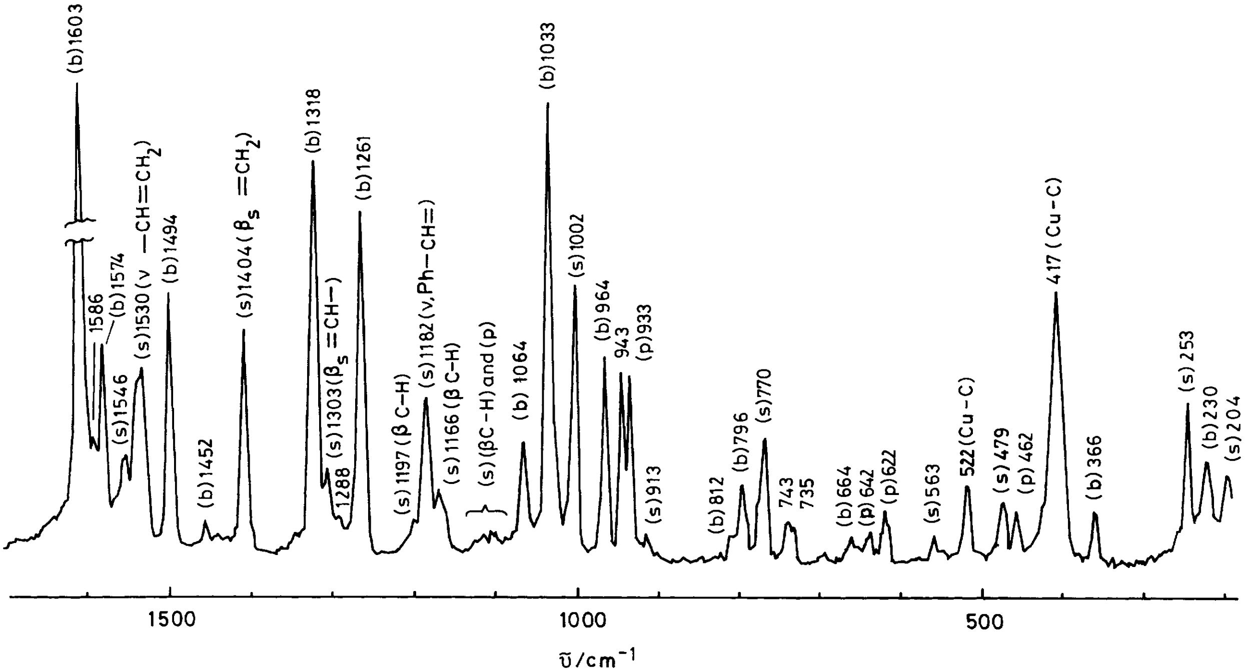


Figure 3. Raman spectrum of [Cu(bipy)(CH$_2$=CHPh)(ClO$_4$)]. All frequencies were tentatively assigned; absorptions marked with (s), (b), and (p) are due to styrene, bipy, and perchlorate anion respectively. The other abbreviations are as in ref. 14 and absorptions without any abbreviations are not assignable

the geometry around the Cu in this complex is essentially trigonal. On the other hand, it has been reported that the Cu^I in $[Cu\{NH(C_5H_4N)_2\}(CO)]ClO_4$ is co-ordinated to two pyridine nitrogen atoms and a carbonyl group in a trigonal-planar arrangement, although it is also weakly co-ordinated to the ClO_4 anion at a distance of 2.429(1) Å.[2] The geometry is considered to be trigonal pyramidal rather than trigonal. More recently, co-ordination of Cl^- to Cu^I has also been reported in a four-co-ordinate complex. The molecular structure of $[Cu(bipy)(CH_2{=}CHPh)(ClO_4)]$ is trigonal pyramidal.[19]

The objective of the present study was to investigate the nature of copper(I)–olefin bonding. Recently, on the basis of structural studies of ethylene complexes, Thompson and co-workers[1,2] implied that the co-ordination mode of ethylene to Cu^I is dominated by σ donation from the ethylene and that π back donation from the Cu^I ion to the ethylene π^* orbital is not of great importance, because of virtually no effect on the C–C bond distances of the bound ethylene molecules. On the other hand, the participation of π back donation has been demonstrated from studies on the formation constants and ^1H n.m.r. spectra of several copper(I)–ethylene complexes, although σ donation is predominant.[3] If π back donation from the d_π orbital of metal to the antibonding π^* orbital of the olefin results in co-ordination, the vinyl group is sure to be affected in the following manner: the C–C bond distance of the co-ordinated olefin is lengthened, the resonances of the olefin nuclei are moved upfield due to the shielding effect,[13] and the C=C stretching frequency in the Raman spectrum decreases.[16] The present complex exhibited a slight lengthening of the C–C bond distance with bending back of the phenyl group from the olefinic plane, upfield shifting of the proton resonances of the vinyl group, and a decrease in the C=C stretching frequency. All these results indicate a decrease in the C=C double-bond character, and thus suggest a contribution from π back donation from Cu^I to the olefin bond as well as from σ donation. The extent to which electrons are transferred to a ligand containing a double bond (π back donation), however, may not be very large, as can be judged by the extent of lengthening of the C–C bond distance, bending back of the phenyl group, upfield shift of the vinyl proton resonances, and decreasing in the C=C stretching frequency.[15]

Acknowledgements

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