

A Novel Copper Complex and CVD Precursor: (η^2 -2-Butyne)copper(I) Hexafluoroacetylacetonate

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The synthesis of (η^2 -2-butyne)copper(I) hexafluoroacetylacetonate was achieved in one step and in good yield. X-ray crystallographic examination revealed two structurally similar, nearly planar molecules within the monoclinic crystal. The 2-butyne ligand is η^2 bonded, parallel to the Cu β -diketonate plane, the methyl groups are cis bent away from copper ($\theta_{\text{CCMe}} = 163^\circ$) with a small angle of deformation from linear and the C \equiv C bond distance averages 1.210 Å. All of the data indicate π -electron donation from the butyne ligand to the copper(I) center and minimal π -back-bonding to the alkyne. This previously unreported complex is a volatile yellow solid which undergoes pyrolytic decomposition to copper metal. Chemical vapor deposition of high-purity copper films with rapid rates of deposition and good conformality were observed upon pyrolytic decomposition from this complex.

Introduction

Chemical vapor deposition of conformal copper films is required for the metallization of multilayered integrated circuits. The ability to fill high-aspect ratio holes requires a technique such as chemical vapor deposition (CVD).¹ Research geared toward the identification and synthesis of volatile metal precursors specifically for chemical vapor deposition (CVD) of high-purity films is actively being pursued. The utility of a specific precursor depends upon the precursor's chemical structure and its resulting chemical and physical properties. For a given precursor, the volatility (partial pressure) will directly influence the rate of film growth, the decomposition temperature will determine the temperature regime required to grow metal films, and the mechanism of pyrolytic decomposition will ultimately determine the film's purity. Other important considerations relate to the long-term stability, ease of preparation, and ultimate cost of the precursor. Also, the reproducible deposition of copper films is a stringent requirement.

Although copper(II) bis(hexafluoroacetylacetonate)²⁻⁵ has historically been used for copper CVD, recent studies have utilized η^5 -cyclopentadienylcopper(I) phosphines,^{6,7} copper(I) alkoxide phosphines,⁷ copper(I) *tert*-butoxide tetramer,⁸ copper(II) fluorinated β -ketoimines,⁹ and Lewis base stabilized copper(I) β -diketonate complexes.¹⁰⁻¹⁵ The

ability to deposit high-purity copper films via pyrolysis of (1,5-cyclooctadiene)copper(I) hexafluoroacetylacetonate^{11a} and related complexes has been reported. These complexes are examples of a broad class of copper(I) β -diketonate complexes which can be used for copper CVD.^{11b} The ability to alter the precursor's structure and physicochemical properties allows one to alter the CVD process via modification of the molecular structure of the precursor.

In this paper, (η^2 -2-butyne)copper(I) hexafluoroacetylacetonate is reported for the first time.^{14,15} X-ray crystallography, nuclear magnetic resonance, and infrared spectroscopies were used to analyze the alkyne-copper interaction. Pyrolytic CVD was utilized to deposit copper films with good conformality and high purity. This complex represents an entirely new class of alkyne-stabilized copper(I) β -diketonate complexes.¹⁵

Experimental Section

The 2-butyne complex was analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The gravimetric data were obtained on an Omnitherm ATvantage II instrument using an open pan which was purged with N₂ and a heating rate of 5 °C/min. The calorimetric data were obtained with a Du Pont Analyst 2100 instrument using a sealed pan with a heating rate of 10 °C/min. Infrared spectra were obtained using an IBM Instruments IR44 single-beam spectrometer. The spectra were obtained by making a pellet of the copper complex in KBr or solutions of (η^2 -2-butyne)copper(I) hexafluoroacetylacetonate in CCl₄. ¹H and ¹³C NMR spectra were obtained on an IBM Instruments 300-MHz spectrometer with automatic sample capability. The ¹³C spectra were obtained using a composite pulsed decoupling (CPD) WALTZ method. A comparison of the spectral data for the "free" ligand and the ligand bound to the copper(I) hexafluoroacetylacetonate complex was made. Mass spectral data were obtained on a Hewlett-Packard 5995 gas chromatograph-mass spectrometer with a direct inlet probe for solids. The peaks are reported in descending abundance, which is given in parentheses.

The synthesis of (η^2 -2-butyne)copper(I) hexafluoroacetylacetonate was achieved in one step by a modification of the literature procedure.¹⁶ A three-neck round-bottom flask was

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charged with 24.0 g (0.168 mol) of Cu_2O (Aldrich) and stirred in 250 mL of spectroscopic grade methylene chloride. 1,1,1,5,5,5-Hexafluoroacetylacetone (25 g, 0.12 mol, Aldrich) was added dropwise to the stirred solution which contained 6.5 g (0.12 mol) of 2-butyne (Aldrich). The reaction was stirred with a magnetic stir bar throughout the addition and for 30 min after the addition was completed. The reaction was carried out under a steady flow of N_2 ; although the complex is slightly O_2 sensitive, it is not necessary to purge or "sparge" the solution prior to initiation of the synthetic reaction. The brick-red cuprous oxide is suspended in the clear solution, and as the reaction proceeds the solution becomes yellow-green. Isolation of the product was achieved by filtering off the excess cuprous oxide and washing several times with CH_2Cl_2 . The filtrate and washes were combined and concentrated by vacuum distillation on a rotary evaporator with a bath temperature of 35 °C. The crude green-yellow product (95%) was purified by vacuum sublimation at 40 °C and 100 mTorr. The sublimed product consisted of yellow needles of purified product, mp = 72 °C (uncorrected). IR (η^2 -2-butyne)Cu hfac in CCl_4 : 2923, 2852, 2057 ($\text{C}\equiv\text{C}$), 1639, 1555, 1529, 1474, 1257, 1210, 1156, 813, 674, 589 cm^{-1} . (η^2 -2-butyne)Cu hfac in a KBr pellet: 3138, 2964, 2056 ($\text{C}\equiv\text{C}$), 1670, 1605, 1530, 1373, 1346, 1256, 1205, 1147, 1028, 795, 674, 669, 609 cm^{-1} . The IR and Raman spectra of 2-butyne have previously been reported.¹⁷ NMR (η^2 -2-butyne)Cu hfac in CDCl_3 : ^1H 2.17 (s, methyl) and 6.08 ppm (s, methine); ^{13}C 6.5 (s, methyl), 81.0 (s, $\text{C}\equiv\text{C}$), 89.0 (s, methine), 117.5 (br quartet, CF_3 , $J = 4.55$ Hz), and 177.4 (quartet, $\text{C}=\text{O}$, $J = 0.455$ Hz) ppm. 2-butyne in CDCl_3 : ^1H 1.71 (s, methyl); ^{13}C 3.3 (s, methyl) and 74.5 (singlet, $\text{C}\equiv\text{C}$). MS 54 (100%), 63 (90), 69 (85), 201 (71), 117 (64), 53 (53), 27 (52), 28 (40), 65 (38), 39 (37), 50 (36), 119 (36), 203 (32), 51 (28), 139 (23), 255 (13), 324 (11, M^+), 91 (10), 104 (9). Two other peaks were noted at 339 (17) and 341 (8); these are believed to be due to a dimeric species which results from high-vacuum removal of 2-butyne during heating of the complex. This may explain both the presence of higher molecular weight peaks and account for a base peak of 54 (2-butyne). Investigations into the formation of dinuclear species are currently underway.¹⁵

The sublimed needles were submitted to Molecular Structure Corp., Woodlands, TX, for X-ray crystallographic analysis. The analysis was performed on a Rigaku diffractometer were graphite-monochromated $\text{Cu K}\alpha$ radiation and a 12-kW rotating anode generator. The data were collected at 23 °C using the ω - 2θ scan technique to a maximum 2θ value of 120.2°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.23° with a takeoff angle of 6.0°. Weak reflections were rescanned (maximum of three scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 400.0 mm.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range of $76.96 < 2\theta < 79.17^\circ$ correspond to a monoclinic cell with the dimensions $a = 4.5820$ (5), $b = 28.200$ (7), $c = 18.203$ (2) Å, $V = 2342.5$ (7) Å³, and $\beta = 95.157$ (8)°. For $Z = 8$ and a formula weight of 324.69, the calculated density is 1.841 g/cm^3 . The successful solution and refinement of the structure lead to a space group of $P2_1/c$ (No. 14) with $R = 0.047$ and $R_w = 0.051$. The standard deviation of an observation of unit weight was 2.85.

Of the 4086 reflections, 3583 were unique ($R_{\text{int}} = 0.024$). The intensities of three representative reflections were measured after every 150 reflections and found to be constant throughout the data collection (no decay correction was needed), indicating crystal and electronic stability. The structure was solved by SHELXS-86. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{\text{C-H}} = 0.95$ Å). The final cycle of full-matrix least-squares refinement was based upon 2500 observed reflections and 326 variable parameters. All calculations were performed

Table I. Selected Intramolecular Distances Involving the Non-Hydrogen Atoms As Determined by X-ray Crystallographic Analysis of (η^2 -2-butyne)Cu hfac Complex^a

atom	atom	dist	atom	atom	dist
Cu(1)	O(1)	1.971 (4)	C(2)	C(3)	1.204 (7)
Cu(1)	O(2)	1.958 (4)	C(3)	C(4)	1.472 (8)
Cu(1)	C(2)	1.963 (5)	O(1)	C(5)	1.250 (6)
Cu(1)	C(3)	1.959 (5)	O(2)	C(8)	1.252 (6)
C(1)	C(2)	1.474 (8)			

^aDistances are in angstroms. The estimated standard deviations in the least significant figure are given in parentheses.

Table II. Selected Intramolecular Bond Angles Involving the Non-Hydrogen Atoms As Determined from the X-ray Crystallographic Analysis of (2-butyne)Cu hfac Complex^a

atom	atom	atom	angle
C(1)	C(2)	C(3)	162.8 (8)
C(2)	C(3)	C(4)	163.0 (6)
O(1)	Cu(1)	O(2)	93.8 (1)
O(1)	Cu(1)	C(2)	150.4 (2)
O(1)	Cu(1)	C(3)	114.7 (2)
O(2)	Cu(1)	C(2)	115.8 (2)
O(2)	Cu(1)	C(3)	151.8 (2)
Cu(1)	O(1)	C(5)	122.9 (4)
Cu(1)	O(2)	C(8)	123.3 (4)
Cu(1)	C(2)	C(1)	125.3 (4)
Cu(1)	C(2)	C(3)	72.0 (4)
Cu(1)	C(3)	C(2)	72.3 (4)
Cu(1)	C(3)	C(4)	124.7 (4)

^aThe angles are in degrees. The estimated standard deviations in the least significant figure are given in parentheses.

using the TEXSAN crystallographic software package of Molecular Structure Corp.

All CVD experiments reported herein were carried out on silicon substrates which were overcoated with a 200-Å layer of sputtered copper. In some cases, the silicon was overcoated with a layer of polyimide. The depositions were carried out in a warm-walled quartz bell jar reactor with a sample stage which was resistively heated between 150 and 225 °C. The sample stage temperature was monitored with a standard thermocouple. The complex was placed in the bottom of the reactor and heated externally. The total pressure in the reactor during deposition was 300 mTorr, and 30 sccm of helium was used as a carrier gas. Film thickness was measured by stylus profilometry (Tencor) after lifting off a strip of the deposited metal. Film resistances were measured with an Alessi four-point probe station (CPS Model) equipped with a Hewlett-Packard 6112A voltmeter. Film purity was determined by Auger electron spectroscopy (AES) at Surface Science Labs in Mt. View, CA. The samples were compared to an evaporated copper film which is presumed to be $\geq 99\%$ atomic purity.

Results and Discussion

The synthesis of (η^2 -2-butyne)Cu (hfac) is readily accomplished in a single step and in high yield by a modification of the reported literature procedure.¹⁶ The molecular structure of sublimed solid product was obtained by X-ray crystallography. Two structurally unique molecules were present which are chemically identical but which are not related by crystallographic symmetry. One of the molecular structures, as determined by X-ray crystallography, is displayed in Figure 1. The two individual molecules result from crystallographic distortion upon packing into the three-dimensional lattice space; this results in a more compact and thermodynamically stable structure. In this paper, the bond lengths and angles for the second chemically identical, asymmetric crystal are reported in parentheses. The pertinent bond lengths and bond angles, for the crystal depicted in Figure 1, are listed in Tables I and II, respectively. Other crystallographic information, including the refinement of the hydrogen

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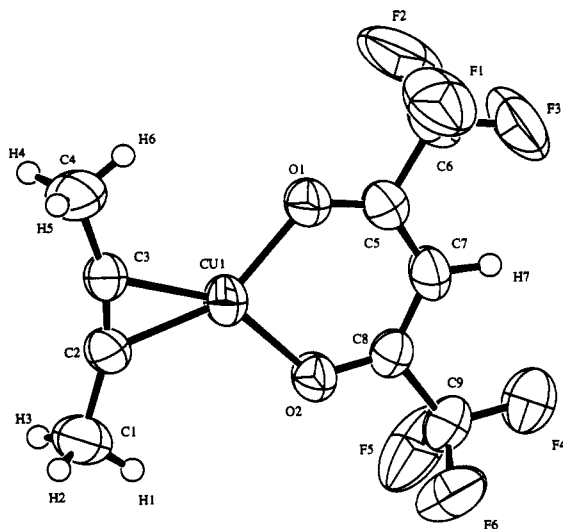


Figure 1. ORTEP plot of one molecule of (η^2 -2-butyne)Cu hfac as determined by X-ray crystallographic analysis.

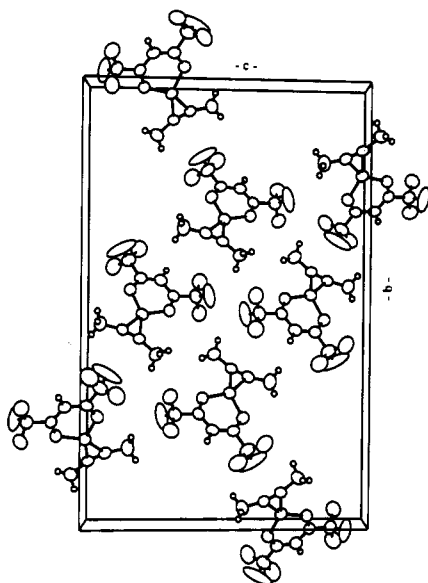


Figure 2. Schematic representation of the bc crystal plane of (η^2 -2-butyne)Cu hfac as determined by X-ray crystallographic analysis.

atomic positions and the atomic parameters for the crystallographic analysis, may be obtained in the supplementary material (see paragraph at end of paper).

The copper-carbon bond distances of the butyne are essentially identical, 1.963 (5) (1.957 (6)) and 1.959 (4) (1.960 (6)) Å for Cu(1)-C(2) and Cu(1)-C(3), respectively. These copper-butyne distances are indicative of equidistant bonding of the 2-butyne to the copper center. The intramolecular bond angles depict a molecule of nearly planar geometry with the 2-butyne very slightly tilted within the plane and parallel to the copper(I) β -diketonate. Figures 2 and 3 display the crystallographic orientation with regard to the three-dimensional crystal planes which are important toward the observed molecular distortion upon crystal packing.

Although mononuclear η^2 -alkyne complexes of Ni,¹⁸ Pt,¹⁹ Pd,²⁰ and Fe²¹ have been reported, mononuclear alkyne

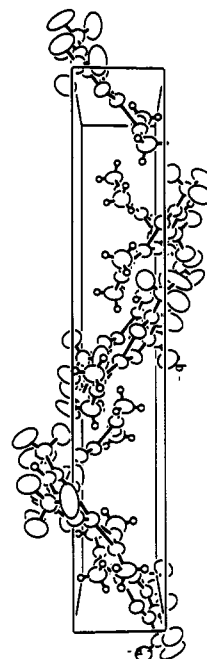


Figure 3. Schematic representation of the ab crystal plane of (η^2 -2-butyne)Cu hfac as determined by X-ray crystallographic analysis.

complexes for copper(I) are less common. An early report²² details a crystal structure of a 2-butyne copper(I) chloride complex which was found to consist of tetrameric units. Other alkyne-copper complexes have been reported to be dinuclear as in the case of bis(trimethylsilyl)acetylenecopper(I) chloride²³ or disubstituted alkyne complexes of copper(I) benzoate.²⁴ Other tetrameric copper complexes, such as 3-hexyne copper(I) trifluoroacetate in which 3-hexyne bridges two copper(I) centers (η^4), have also been reported.²⁵ A copper(I) sandwich complex, bis(trimethylsilyl)acetylenecopper(I) η^5 -cyclopentadiene, was too unstable for crystallographic analysis but was believed to exist as a mononuclear species based upon its spectral characteristics.²⁶ Other η^2 -alkyne-copper complexes which are mononuclear have been reported in mixed metal complexes²⁷ and in tetrafluoroborate ionic complexes.²⁸

Alkyne-copper bonding can be qualitatively described by Dewar-Chat-Duncanson (DCD) theory in a manner analogous to alkene-metal bonding.^{29,30} Upon coordination of an alkyne to a transition metal, the alkyl substituents on the alkyne moiety assume a cis bent geometry (bent away from the metal center) and usually the C \equiv C bond is lengthened (decreased bond order).³¹ In the

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present case, the average C≡C bond length is not lengthened in the complex, 1.204 (7) (1.215 (7)) Å as opposed to 1.211 Å in free 2-butyne.³² Further, the bond lengths of the methyl groups are only slightly elongated, 1.474 (8) (1.481 (8)) and 1.472 (8) (1.468 (8)) Å relative to the "free" butyne (1.457 Å).³² The observed angle of alkyl deformation is extremely small as shown in Table II (17° deformation from linear; $\theta_{\text{CCMe}} = 163.0$ (6) (163.1 (7)) and 162.8 (6) (162.6 (6))°). In fact, this may be one of the smallest angles of deformation reported in a mononuclear η^2 -alkyne-copper complex. The angles of deformation are indicative of the degree of π -back-bonding in the complex;^{31,33} complexes with dominant σ bonding (π -orbital donation from the alkyne to the metal) display nearly normal C≡C bond distances and relatively small angles of deformation upon complexation. Mason³¹ has reported C≡C bond lengths of 1.39 Å and θ_{CCR} of 140° for cobalt and platinum complexes in which π -back-bonding is dominant. In the latter case, the lengthened alkyne bond correlates well with the excited-state geometries of the alkyne and supports the notion of electron donation from the metal to the excited state (π^*) orbitals of the alkyne.^{31,33} Lastly, the strong electron-withdrawing ability of the fluorinated β -diketonate ligand may be largely responsible for the small π -back-bonding component, due to a decreased electron density on the copper(I) center, and almost negligible perturbation of the 2-butyne upon complexation.

The degree of π -back-bonding in the alkyne-metal complex can also be evaluated by vibrational spectroscopy (IR and Raman) and by nuclear magnetic resonance (NMR) spectral shifts. In electron-rich transition metals, the bond order is reduced upon complexation, and shifts in the C≡C stretch are observed in the IR.³¹ A comparison of the infrared frequency for the C≡C stretch in the complex and in the uncoordinated alkyne affords a measure of the alkyne-metal bond. For small $\Delta\nu$ in the C≡C stretch, the alkyne is thought to be σ bound, while in strongly π -back-bonded complexes the $\Delta\nu$ can be as large as 200–400 cm^{-1} (ref 31) or larger.³⁴ In the 2-butyne complex, the change in the C≡C stretch³⁵ is small; $\Delta\nu = 176 \text{ cm}^{-1}$ upon comparison of the Raman-active C≡C stretch in "free" 2-butyne (2233 cm^{-1})¹⁷ and (η^2 -2-butyne)Cu hfac in CCl_4 solution. Although this shift is relatively small, other asymmetric alkynes display similar IR shifts upon coordination to Cu(I) hfac,¹⁵ and this observation is consistent with the negligible increase in the C≡C bond length obtained from the crystallographic data.

NMR spectral shifts for (η^2 -2-butyne)Cu hfac were examined in two solvents. In both solvents, deshielding was observed for the alkyne carbons, the methyl carbons, and the methyl protons. In CDCl_3 , the $\Delta\delta$ ^{13}C was +3.2 (methyl groups) and +6.6 (C≡C) ppm. In the ^1H spectrum, the methyl group hydrogens are deshielded ($\Delta\delta = +0.46$). In $\text{THF-}d_6$ solvent, similar deshielding effects are observed upon coordination; $\Delta\delta$ $^{13}\text{C} = +15.1$ ppm for the alkyne carbons and 3.1 ppm for the methyl carbons. For the ^1H spectrum, $\Delta\delta = +0.42$ ppm for the methyl hydrogens. Deshielding effects for other alkyne-metal complexes have been reported.³⁶ In general, ^{13}C shifts ($\Delta\delta$ C≡C) below

100 ppm are associated with two-electron donation from the alkyne to the metal center, whereas shifts greater than 100 ppm are observed for η^4 complexes. Also, an analysis of shielding and deshielding effects in the ^1H and ^{13}C NMR spectra for a series of alkene and diene complexes of copper(I) hexafluoroacetylacetonate³⁷ and copper(I) triflates³⁸ have been reported. Nevertheless, deshielding of the alkyne carbons observed by NMR, in conjunction with the IR and X-ray crystallographic data, confirms two-electron donation from the alkyne to the copper(I) center.

Thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) were employed to evaluate the stability and thermal transitions (i.e., melting and decomposition) of (η^2 -2-butyne)Cu hfac. The thermal analysis displays a melting endotherm at 72 °C, and the onset of decomposition occurs near 150 °C. Thermogravimetric analysis exhibited a 50% weight loss at 110 °C which is a measure of the volatility of the complex at elevated temperatures. In a separate experiment, the partial pressure of (η^2 -2-butyne)Cu hfac was measured; the complex displayed a vapor pressure of 34 mT at 23 °C and was found to be more volatile than Cu(hfac)₂ complex^{3,11a} even at elevated temperatures. Lastly, the stability of the complex is good, although some O₂ sensitivity of the sublimed crystals was observed upon prolonged standing in air. After 30–40 min, the crystals darken and taken on a copper metal appearance. This O₂ sensitivity is more rapid in organic solutions.

Deposition of copper films via the pyrolytic decomposition of (η^2 -2-butyne)copper(I) hexafluoroacetylacetonate was carried out in a warm-walled bell jar reactor. The substrate was resistively heated to between 150 and 225 °C. The precursor was externally heated to 60 °C, although deposition does occur without external heating. The pressure during deposition was maintained at 300 mT and a He carrier gas flow of 30 sccm was utilized. Under these reactor conditions, a copper film was grown at an average rate of 2033 Å/min and displayed an electrical resistivity of 1.93 $\mu\Omega$ cm. Faster deposition rates have recently been reported from this same precursor under different reactor conditions.¹⁴

As exemplified by the film resistivity, the pyrolytic decomposition of (η^2 -2-butyne)Cu hfac results in the formation of high-purity copper films. As depicted in Figure 4, Auger analysis confirmed the film's purity and argon ion sputtering was used to depth profile the film. The film was calibrated to an evaporated copper standard; after calibration of the film to the standard, the purity of copper is placed at 98 at. % copper. The deposition of high-purity copper films is believed to result from disproportionation of two copper(I) precursors.³⁹ This was confirmed by identification of 2-butyne and copper(II) bis(hexafluoroacetylacetonate) as major byproducts of the decomposition reaction. These two reaction products were isolated from the cold trap after CVD and identified by IR spectroscopy upon comparison with authentic samples.

The deposited copper films displayed excellent uniformity and conformality over the substrate surface. The film morphology was determined by the substrate temperature during deposition. For example, fine-grained mirrorlike films were formed at 150 °C. At higher substrate temperatures, the grain size was observed to increase. Under certain reactor conditions and reduced

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(35) The sharp absorbance centered at 2057 cm^{-1} is believed to be the C≡C stretch. Raman spectra are currently being acquired to conclusively assign this peak. The IR activity of this vibration may be reduced as a result of the small alkyl deformation from the linear geometry.

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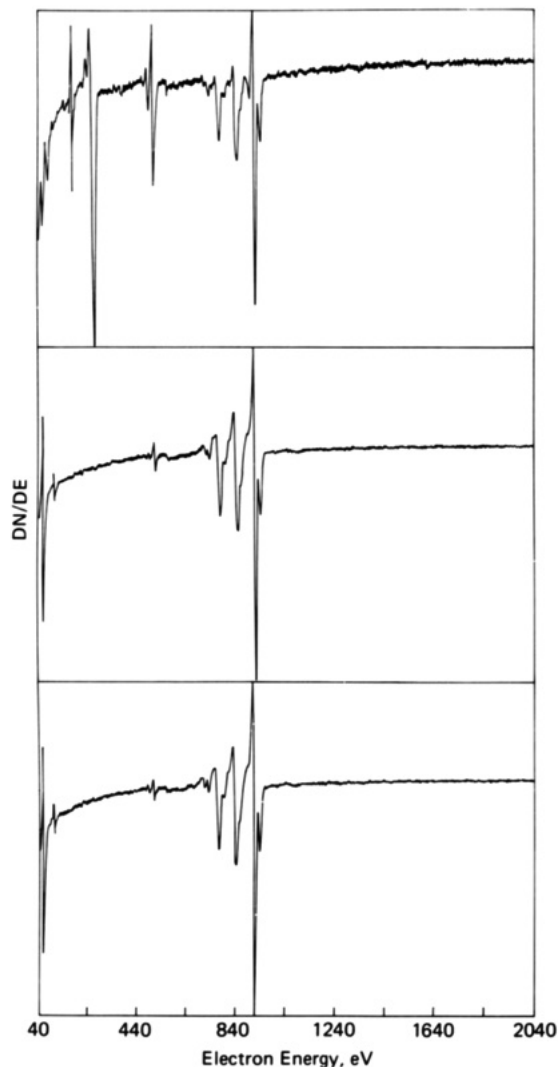


Figure 4. Auger electron spectroscopic data for a copper film deposited from (2-butyne)Cu hfac complex upon pyrolytic decomposition; as received (top), after 100 Å (middle), and after 200 Å (bottom) depth profiling with argon.

substrate temperatures (150 °C), selective copper growth¹² was observed on metal features (Co, Mo) as opposed to dielectrics such as silicon dioxide or polyimide. For some process conditions, the deposited films also display good conformality over surface features. An example of a conformal copper film deposited at a lower rate of deposition is shown in Figure 5. The sample was physically cleaved to examine the hole fill of micron-sized holes. As is evident in Figure 5, the holes are readily filled using this precursor.

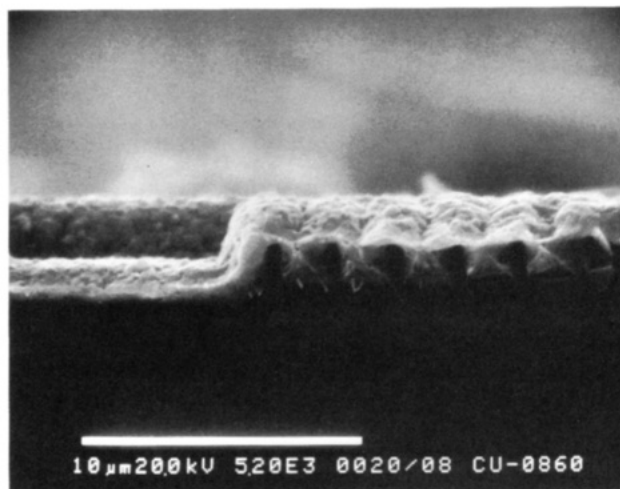


Figure 5. Scanning electron micrograph of a copper film deposited upon pyrolytic decomposition of (η^2 -2-butyne)Cu hfac. The sample was physically cleaved to examine step coverage. The deposited copper film displays good conformal coverage over the surface features and readily fills micron-sized via holes.

Conclusions

The synthesis, X-ray crystallographic molecular structure, and pyrolytic decomposition of (η^2 -2-butyne)Cu(I) hfac complex is reported. In the molecular structure, 2-butyne is η^2 bonded and parallel to the Cu β -diketonate plane. The molecule is essentially planar with strong electron donation from the alkyne to the copper(I) center. A very small angle of methyl deformation is observed and indicates minimal π -back-bonding to the butyne. Pyrolytic decomposition leads to the deposition of high-purity copper films which display good conformality. As a result of the complex's volatility, rapid rates of copper film formation are observed. This complex represents a general class of copper(I) β -diketonate complexes which are stabilized via η^2 bonding of alkynes to the copper center.

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Supplementary Material Available: Tables of refinement of the hydrogen atom positions and the atomic parameters for the crystallographic analysis (15 pages). Ordering information is given on any current masthead page.