for 45 min and 0.727 g (5.34 mmol) of enone IX[1] in 5.0 ml of THF was added over 12 min. After stirring for 30 min at this temperature, the reaction mixture was warmed to −40° during 15 min and then quenched by pouring into ice-cold saturated aqueous ammonium sulfate. The organic layer was separated and the aqueous layer was extracted with ether. The combined ethereal layers were extracted with 2% (v/v) sulfuric acid, filtered through a pad of hyflo super cel, and dried ($MgSO_4$) to afford, after removal of solvent, 7.77 g of yellow-brown oil. Column chromatography on alumina with hexane as eluent gave 3.14 g (91%) of tetra-*n*-butyltin. Further elution with $CHCl_3$ yielded 4.07 g (93%) of the desired ketone XI: ir (neat, partial) 3.39, 5.84, 6.30, 10.1, and 10.4 μ; nmr (CCl_4) δ 0.27–2.85 (br m with s at 2.25, total 40 H) and 5.84 (s, 2 H); *m/e*, 452.2255 (calcd for $C_{23}H_{42}O^{118}Sn$, 452.2253).

1-Ethynylbicyclo[4.3.0]nonan-3-one (XIII). A solution of 0.233 g (0.50 mmol) of 1-(*trans*-2-tri-*n*-butylstannylethenyl)bicyclo[4.3.0]nonan-3-one (XI) in 5 ml of dry acetonitrile was treated with 0.232 g (0.52 mmol) of lead tetraacetate. The reaction mixture became homogeneous after 3 min and then began forming a brown precipitate. After stirring at room temperature for 3 hr, tlc analysis ($CHCl_3$) showed no starting material. Dilution of the crude product with pentane and filtration through Celite and alumina (each pad washed twice with pentane and once with methylene chloride) afforded almost pure 1-ethynylbicyclo[4.3.0]nonan-3-one (XIII) (51 mg, 64%), homogeneous by tlc analysis (R_f 0.44, $CHCl_3$): ir (neat, partial) 3.03, 3.38, 4.74, and 5.85 μ; nmr (CCl_4) δ 0.50–2.57 (br m with s at 1.96, 2.10, and 2.38); *m/e* 162.1045 (calcd for $C_{11}H_{14}O$, 162.1049).

The methodology reported here leads to compounds which are otherwise relatively inaccessible. Numerous applications can be foreseen in addition to the synthesis of angularly substituted polycyclic structures.[13]

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E. J. Corey,* Robert H. Wollenberg
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received May 24, 1974

Resonance Raman Studies of "Blue" Copper Proteins

Sir:

"Blue" copper proteins[1] have at least one copper which gives rise to unusually intense visible absorption bands and low hyperfine coupling constants. Although these atypical properties have prompted many spectroscopic, magnetic, and theoretical investigations, little is known about the specific ligands bound to copper. We report herein the resonance Raman[2] (RR) spectra between 1700 and 200 cm^{-1}, of "blue" copper in human ceruloplasmin and in *Rhus vernicifera* stellacyanin and laccase. RR spectra of copper ovotransferrin as well as vibrational spectra of amino acids and copper complexes are used to interpret the protein spectra and formulate a molecular basis for copper–ligand bonding in the "blue" copper proteins.

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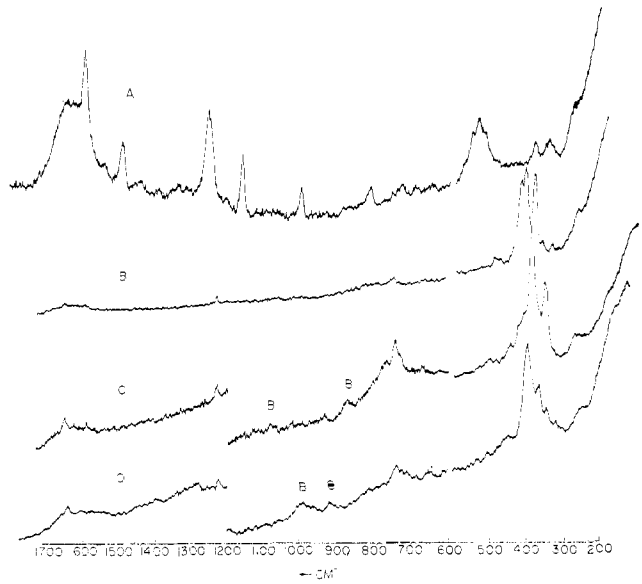

Figure 1. Resonance Raman spectra of Cu(II) ovotransferrin, 44.6 mg/ml of protein, in 0.03 *M* $NaHCO_3$, pH ~8.0 (A); laccase, 10.9 mg/ml, in 0.05 *M* phosphate buffer, pH 5.5 (B); stellacyanin, <600 cm^{-1}, 3.3 mg/ml, >600 cm^{-1}, 8.4 mg/ml, in 0.05 *M* phosphate buffer, pH 5.5 (C); and ceruloplasmin, 11.6 mg/ml, in 0.05 *M* acetate buffer, pH 5.5 (D). Experimental conditions (time constant, 5 sec; scan rate, 30 cm^{-1}/min)

	Excitation (nm)	Power (mW)	Slit width (cm^{-1})	Sensitivity (counts/sec)
A	488.0	70	8.6	1000
B	647.1	70	6.4	1000
C	647.1	80	7.0	1000
D	647.1	80	10.0	2000

Broad bands near 880, 920, 1000, and 1080 cm^{-1} marked with a B are due to buffer.

Standard methods were followed for the isolation of stellacyanin[3] and laccase,[3] further purification of ceruloplasmin[4] (Schwartz–Mann), and conversion of apo-ovotransferrin (three times crystallized, provided by Dr. D. H. Morris) to the Cu(II) complex.[5]

Excitation into the ~600-nm electronic absorption band with the 647.1-nm Kr^+ (or 568.2-nm Ar^+) laser line yields Raman spectra (Figure 1) showing intensity-enhanced vibrations (depolarization ratios, 0.3–0.4) below 450 cm^{-1} from "blue" copper. Some weakly enhanced ligand vibrations are detected in the region from 450 to 1700 cm^{-1}. The RR spectrum of Cu(II) transferrin irradiated within the 440-nm electronic absorption band by the 488.0-nm Ar^+ line shows intense resonance-enhanced ligand modes above 450 cm^{-1} as well as some less intense low-frequency bands.

Tyrosine oxygen and imidazole nitrogen (from histidine) bonding to Fe(III) has been established in Fe(III) ovotransferrin.[5] In the region 600–1700 cm^{-1}, the RR spectrum of Cu(II) transferrin has the same features (including intense ligand vibrational bands of tyrosine) as the Fe(III) complex.[6] In contrast, low-frequency metal–ligand vibrations dominate the RR spectra of

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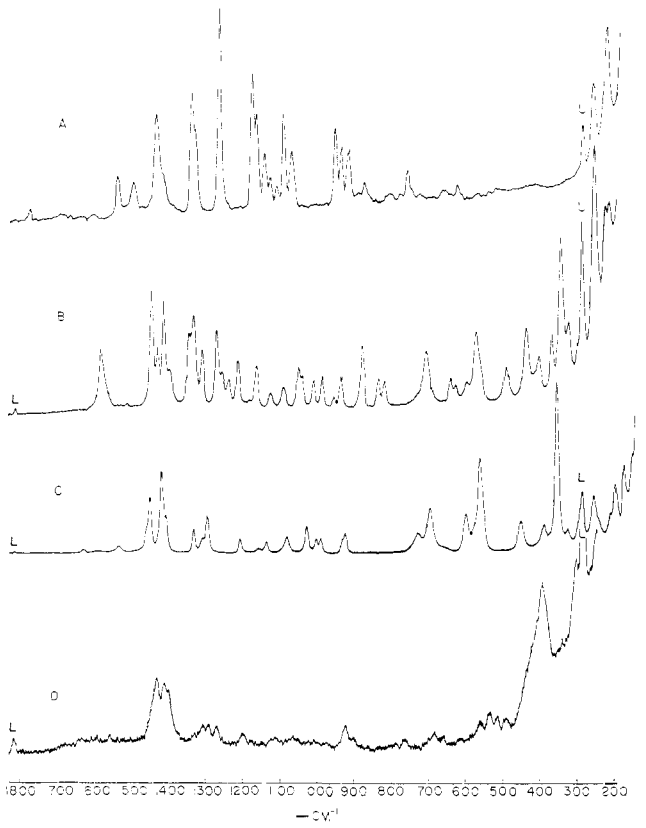


Figure 2. Raman spectra of bis(imidazolato)copper(II) (A), (glycyl-L-histidinato)copper(II) trihydrate (B), glycylglycinatocopper(II) sesquihydrate (C), and disodium glycylglycylglycylglycinatocuprate(II) decahydrate (D) as powdered solids. Experimental conditions (time constant, 5 sec; scan rate, 30 cm^{-1}/min)

	Excitation (nm)	Power (mW)	Slit width (cm^{-1})	Sensitivity (counts/sec)
A	441.6	70	7.4	8,000
B	441.6	40	7.4	4,000
C	441.6	40	5.1	10,000
D	441.6	80	9.7	1,000

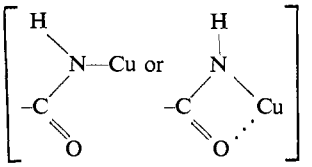
L, laser plasma line.

ceruloplasmin, stellacyanin, and laccase. Tyrosine oxygen can thus be excluded as a ligand for "blue" copper in these proteins.

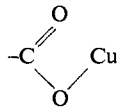
Stellacyanin contains a single "blue" copper atom and shows weak vibrational bands near 750, 1240, and 1650 cm^{-1}. These bands recur in the many copper proteins, laccase, and ceruloplasmin. Weak bands could appear from the normal Raman spectrum of the protein superimposed on the resonance Raman spectra. However, irradiation of the "blue" copper proteins with 457.9- and 488.0-nm Ar^+ laser lines, under the same conditions as for 568.2- and 647.1-nm excitation, produced neither resonance spectra nor normal Raman bands near 750, 1240, or 1650 cm^{-1}. The colorless reduced copper proteins do not show Raman bands at these frequencies either.

Numerous Cu(II)–peptide complexes[7] have been synthesized and structurally characterized. In general, the amino and carboxyl terminal groups participate in metal bonding together with peptide nitrogen and occasionally carbonyl oxygen. We have measured Raman spectra (441.6-nm Cd laser) of Cu(II) complexes with imidazole,[7] glycyl-L-histidine,[8] glycylglycine,[7] and glycylglycylglycylglycine[9] (Figure 2). Raman bands of these complexes were not intensity enhanced by excitation (647.1 nm Kr^+) into the weak ligand field absorption band ($\epsilon \sim 100\ M^{-1}\ cm^{-1}$) near 600 nm. By using the vibrational models cited, we propose the following tentative assignments for the RR bands of "blue" copper proteins.

Peptide complexes with Cu–N (peptide, deprotonated nitrogen) bonds show an intense Raman band near 400 or 350 cm^{-1} (Figure 2, B, C, D), which is assigned to ν(Cu–N). Cu–O (carbonyl) stretching vibrations as in biuret complexes[10] can occur in the same frequency region. Thus, the intense RR bands in the "blue" copper proteins are assigned to similar Cu–N and possibly Cu–O stretching vibrations. The weakly enhanced band between 1640 and 1660 cm^{-1} is assigned to a C=O vibration either from a peptide carbonyl (adjacent to a deprotonated and coordinated peptide nitrogen,[11] –C(=O)N–Cu, or directly bonded to copper as in glycylglycylglycinatocopper(II) chloride sesquihydrate[12]) or an amide carbonyl, asparagine or glutaamine residue



Assignment to a C=O vibration near 1650 cm^{-1} from a coordinated carboxylate



is unlikely since the high frequency carboxylate stretching vibration[13] in the Raman spectra of Cu(II)–glycylglycine and Cu(II)–glycine occurs at 1590 cm^{-1}. Moreover, in these complexes the intensity of the 1590-cm^{-1} band is weak compared to the carboxylate mode near 1400 cm^{-1}. The 1240-cm^{-1} "blue" copper band is tentatively assigned to a C–N (peptide) stretch or amide III mode[14] deriving its intensity enhancement from one of the types of Cu–amide coordination outlined above. In these ligands the double bond character of the C–N bond should be greater than C^2–N in *N*-methylacetamide[15] ($CH_3C^1ONHC^2H_3$, $\nu(C^2\text{–}N)$ at 1120 cm^{-1}) but probably lower than C–N in deuterated polyglycines[14] (amide II′ at 1460 cm^{-1}) or $CD_3C^1ON(CD_3)_2$[16] ($\nu(C^1\text{–}N)$

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at 1430 cm^{-1}). RR bands between 700 and 800 cm^{-1} and some weaker bands near 500 cm^{-1} in "blue" copper proteins could originate from carbonyl bending modes, δ (C=O), and the shoulder at ~260 cm^{-1}, from a Cu–N (imidazole) vibration (by comparison with A and B, Figure 2) or a Cu–S(cys) vibration.[17] Other weak bands near 450 and 330 cm^{-1}, yet to be assigned, may arise from bending modes, δ(CNC) or δ(CCN).

The number of coordinating ligands in "blue" copper is unknown; however, the presence of low energy electronic absorption (800–900 nm) suggests a five-coordinate[18] or flattened tetrahedral[19] geometry. Core structures of the type CuN_3S, CuN_4S or CuN_2OS, and CuN_3OS where N (amide), S (cysteine), and O (carbonyl) are ligands appear to be the most favored. The presence of a sulfur atom provides a logical mechanism for the intensification (analogous to the intensity enhancement of the spin-forbidden $^6A_1 \rightarrow {}^4T_1$, band[20] of $Fe^{III}S_4$ in rubredoxin and spinach ferredoxin) of the "blue" copper ligand field bands.

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Olavi Siiman, N. Martin Young, Paul R. Carey*
Division of Biological Sciences
National Research Council of Canada[21]
Ottawa, Ontario, Canada K1A OR6
Received April 4, 1974

Synthesis and Infrared Spectroscopic Detection of Rhenium Pentacarbonyl

Sir:

The $Re(CO)_5$ radical was first detected by Junk and Svec[1] in a mass spectroscopic study of $Re_2(CO)_{10}$ vapor. These data yielded useful information concerning the Re–Re and Re–C bond dissociation energies. More recently, Wrighton and Bredesen[2] have investigated the photoreaction of $Re_2(CO)_{10}$ with CCl_4 and have provided evidence for an efficient homolytic fission mechanism and a $Re(CO)_5$ radical intermediate. In this context it is noteworthy that a variety of stable, paramagnetic phosphine substituted carbonyls[3–6] have been prepared from photochemical and thermal reactions of $Re_2(CO)_{10}$ with substituted phosphines, examples being *trans*-$Re(CO)_3(P(C_6H_5)_3)_2$ and *cis*-$Re(CO)_3(MeP(C_6H_5)_2)_2$. However, vibrational, uv–visible and ESR spectroscopic data have not previously been reported for $Re(CO)_5$, all of which are capable of yielding pertinent information concerning the nature of the bonding and the molecular and electronic structure of the radical.

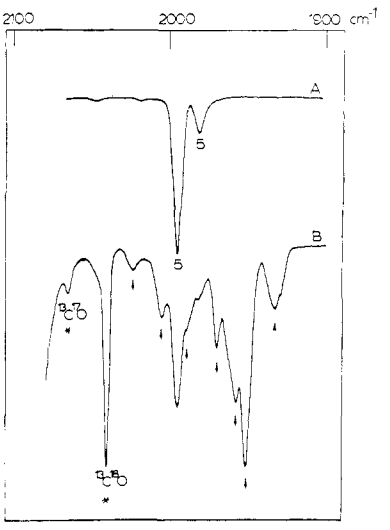

Figure 1. Matrix infrared spectrum of the products of the cocondensation reaction of Re atoms with (A) $^{12}C^{16}O/Ar \cong 1/10$ and (B) $^{12}C^{16}O/^{13}C^{16}O/Ar \cong 1/1/20$ at 10°K.

Our previous experiences with metal atom synthetic techniques[7] have led us to believe that cocondensation reactions in *reactive* matrices favor the product with highest stoichiometry, examples being $Pt(CO)_4$,[8] $Ni(N_2)_4$,[9] and $Pd(O_2)_2$,[10] suggesting that a direct preparative route to $Re(CO)_5$ could be through the Re atom CO matrix reaction. In this communication we report preliminary matrix infrared spectroscopic data which show that this is indeed the case. Using the matrix infrared set-up and furnace arrangement described previously,[11] Re atoms were cocondensed with pure $^{12}C^{16}O$ at 15°K. With a CO:Ar ≅ 1:10 matrix and a 20°K deposition, it was found that sufficient matrix diffusion of CO occurred to yield a spectrum essentially the same as that observed in pure CO. The infrared spectra of the product (Figure 1A) shows *two* major lines at 1995 (s) and 1977 (w) cm^{-1} with absorption intensities approximately 4:1, respectively. These lines retained the same relative intensities during matrix depositions and warm-up experiments indicating that they belong to a *single* species. The spectrum obtained is quite distinct from that of matrix isolated $Re_2(CO)_{10}$ in Ar which is shown in Table I for the purposes of comparison.

The general pattern of CO stretching modes compared to $Mn(CO)_5$[12] and $Cr(CO)_5^-$ [13] and the general shift to lower frequencies compared to $Re_2(CO)_{10}$ strongly suggest that the product of the Re–CO reaction is $Re(CO)_5$ with a square pyramidal molecular struc-

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