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Raman and Extended X-ray Absorption Fine Structure Characterization of a Sulfur-Ligated Cu(I) Ethylene Complex: Modeling the Proposed Ethylene Binding Site of *Arabidopsis thaliana* ETR1

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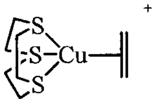
Introduction

The hormone ethylene is involved in many important phases of plant development including germination, growth, aging, and the separation of leaves or fruits.[1] Direct study of ethylene receptors has proved challenging because of their low cellular concentration and membrane localization. There are, however, many examples of synthetic complexes designed to model the active site of ethylene receptors.[2] All of these models incorporate a Cu(I) ion bound to ethylene in the presence of aliphatic or aromatic amine donor ligands. Recently, significant advances have been made in elucidating the structure of ETR1, an ethylene receptor from *Arabidopsis thaliana*.[3] ETR1, when overexpressed in yeast cells, requires copper ion for high-affinity ethylene binding, providing the first direct evidence that copper is involved in ethylene binding in a receptor protein. Several amino acids in the membrane-spanning region of ETR1 are essential for ethylene binding activity, most notably histidine 69 and cysteine 65. Alteration of either residue leads to complete elimination of ethylene binding, suggesting that together they may act to ligate the copper cofactor. These data imply that biologically relevant models of the ethylene receptor should include sulfur ligation. We report herein the synthesis and characterization of the first sulfur-ligated Cu(I)−ethylene complex $[Cu([9]aneS_3)(C_2H_4)]^+$ (**1**) and its CO analogue $[Cu([9]aneS_3)(CO)]^+$ (**2**).



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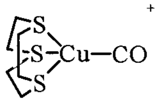

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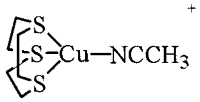

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Experimental Section

General Methods. Reactions were carried out using Schlenk techniques. $[Cu(CH_3CN)_4][PF_6]$ was prepared according to literature methods.[4] Solvents were dried and distilled under N_2 prior to use. Ethylene (Polymer grade, Matheson), CO (99.5%, AGA), and isotopically labeled gases (Aldrich) were used without further purification. $[Cu(H_2O)_6][BF_4]_2$ was purchased from Strem.

Synthesis of $[Cu([9]aneS_3)(C_2H_4)][BF_4]$ (1[BF$_4$]). Method 1. $[Cu(H_2O)_6][BF_4]_2$ (0.069 g, 0.2 mmol) was dissolved in 10 mL of degassed acetone. A 2 in. piece of coiled copper wire was suspended in the blue solution by a string, and the solution was stirred under 1 atm of ethylene gas for 12 h. The resulting colorless copper solution was cooled to −78 °C, and the copper wire was removed under gas purge. A solution of 0.072 g (0.4 mmol) of $[9]aneS_3$ in 2 mL of acetone was added dropwise via syringe with fast stirring. Diethyl ether (30 mL) was added to precipitate the white product **1**$[BF_4]$, which was collected by filtration under an ethylene atmosphere (0.054 g, 75%). **2**$[BF_4]$ was prepared similarly from $[Cu(H_2O)_6][BF_4]_2$ (0.069 g, 0.2 mmol), using a CO atmosphere in place of ethylene (0.042 g, 58%).

Synthesis of $[Cu([9]aneS_3)(CH_3CN)][PF_6]$ (3[PF$_6$]). $[Cu(CH_3CN)_4][PF_6]$ (0.744 g, 2.0 mmol) was dissolved in 10 mL of acetone. $[9]aneS_3$ (0.360 g, 2.0 mmol) was added as a solid with fast stirring. The product, **3**$[PF_6]$, was precipitated upon addition of 30 mL of diethyl ether (0.822 g, 96%). **3**$[PF_6]$ is readily recrystallized from acetone/ether. Anal. Calcd for $C_8H_{15}CuF_6NPS_3$: C, 22.35; H, 3.52; Cu, 14.78; N, 3.26; S, 22.37. Found: C, 22.58; H, 3.64; Cu, 15.42; N, 3.41; S, 21.58.

Synthesis of $[Cu([9]aneS_3)(C_2H_4)]$ (1[PF$_6$]). Method 2. 3$[PF_6]$ (0.109 g, 0.25 mmol) was dissolved in 10 mL of acetone. The solution was cooled to −78 °C, and ethylene was bubbled through it for 10 min. Upon addition of 30 mL of diethyl ether, a white precipitate formed. The product **1**$[PF_6]$ was isolated by vacuum filtration under an ethylene atmosphere (0.087 g, 84%). Anal. Calcd for $C_8H_{16}CuF_6PS_3$: C, 23.04; H, 3.86; Cu, 15.24; S, 23.07. Found: C, 23.64; H, 4.06; Cu, 14.96; S, 24.54. The CO complex was prepared similarly, with CO replacing ethylene, from 0.142 g of **3**$[PF_6]$, yielding **2**$[PF_6]$ (0.092 g, 68%). Anal. Calcd for $C_7H_{12}CuF_6OPS_3$: C, 20.16; H, 2.89; Cu, 15.24; S, 23.07. Found: C, 19.54; H, 3.14; Cu, 15.57; S, 23.92.

Spectroscopic Characterization. Raman spectra were collected on solid samples of **1**−**3** packed in glass capillary tubes. Raman scattering was excited with either 10 or 20 mW of 514.5 nm light that was passed through a 10 nm dielectric band-pass filter (Corion). Scattered light was collected at 90° with an *f*/1.1 lens and focused at *f*/7.8 into a scanning double monochromator (Spex 1403). The resolution at the detector was set to 1 cm^{-1}; the monochromator's two intermediate slits were opened to their maximum width of ∼3.5 mm. An external filter (SuperNotch-Plus, Kaiser Optical Systems) was used to remove residual laser lines. Detection was accomplished with a backthinned 1024 × 256 pixels (26.6 mm × 6.7 mm) charge-coupled device (ISA CCD2000).

Cu K-edge extended X-ray absorption fine structure (EXAFS) data were collected at Stanford Synchrotron Radiation Laboratory (SSRL) on eight-pole wiggler BL7-3: ring conditions 3.0 GeV, 60−100 mA; Si(220) double-crystal monochromator, detuned 50% to reject harmonics; transmission measurements of diluted solid samples at 10 K using nitrogen-filled ion chambers; internal Cu foil energy calibration, first inflection point assigned to 8980.3 eV. The presented data represent the average of three and two scans for **1** and **2**, respectively. Data were

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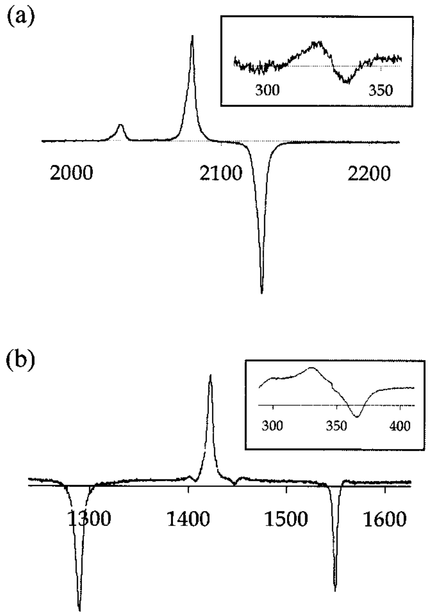

Figure 1. Raman difference spectra of **2** and **1**. Shown are (a) carbonyl and M−C regions (M−C region is in the inset) of [Cu([9]aneS$_3$)($^{12}C^{16}O$)][PF$_6$] subtracted from a mixture of [Cu([9]aneS$_3$)($^{13}C^{16}O$)][PF$_6$] and [Cu([9]aneS$_3$)($^{13}C^{18}O$)][PF$_6$] and (b) C═C and M−C$_2$H$_4$ regions (M−C$_2$H$_4$ region is in the inset) of [Cu([9]aneS$_3$)(C$_2$H$_4$)][PF$_6$] subtracted from [Cu([9]aneS$_3$)(C$_2$D$_4$)][PF$_6$].

analyzed with EXAFSPAK[5] using ab initio phase and amplitude parameters generated with FEFF, version 6.0.[6]

Results and Discussion

The ethylene complex **1** and the carbonyl complex **2** were prepared and isolated as stable crystalline solids according to two different procedures. In the first procedure, [Cu(H$_2$O)$_6$][BF$_4$]$_2$ and Cu metal were combined under an ethylene or CO atmosphere. A color change from blue to colorless indicated the completion of the comproportionation. A solution of [9]aneS$_3$ was added, and **1**[BF$_4$] or **2**[BF$_4$] was precipitated as a white solid by addition of diethyl ether. The second procedure involved displacement of CH$_3$CN from [Cu([9]aneS$_3$)(CH$_3$CN)]$^+$ (**3**) by ethylene or CO. The starting material, **3**[PF$_6$], was prepared by reaction of [Cu(CH$_3$CN)$_4$][PF$_6$] with 1 equiv of [9]aneS$_3$ in acetone. Isolated **3**[PF$_6$] was characterized by Raman and NMR spectroscopy. **3**[PF$_6$] exhibits a characteristic single sharp CN stretch at 2273 cm^{-1}, distinct from that of [Cu(CH$_3$CN)$_4$][PF$_6$]. For preparation of **1**[PF$_6$] or **2**[PF$_6$], **3**[PF$_6$] was dissolved in acetone and cooled to −78 °C. Ethylene or CO gas was introduced, and the product **1**[PF$_6$] or **2**[PF$_6$] was precipitated with diethyl ether. This latter method was also used to prepare the isotopically labeled complexes [Cu([9]aneS$_3$)(C$_2$D$_4$)][PF$_6$] and [Cu([9]aneS$_3$)(^{13}CO)][PF$_6$].

Complex **2** was characterized by solid-state Raman spectroscopy and ^{1}H and ^{13}C solution NMR spectroscopy.[7] In the Raman spectrum of **2**, an intense band is observed at 2123 cm^{-1}. A shift to 2081 cm^{-1} upon incorporation of $^{13}C^{16}O$ and to 2033 cm^{-1} with $^{13}C^{18}O$ (Figure 1a) allows assignment of this band to a CO stretch.[8] A weak, low-frequency mode at 334 cm^{-1}, which shifts to 323 cm^{-1} with $^{13}C^{16}O$ (Figure 1a, inset), is tentatively assigned to the M−C stretch. The M−C stretch for the $^{13}C^{18}O$ isotopomer is not observed presumably because of its low intensity. Vibrational modes of the macrocycle and counterion are also observed. The structure and position of the macrocycle peaks are distinct from those of the free macrocycle and are consistent with a pseudo-3-fold trisulfur linkage to copper. Solution (acetone-d_6) ^{1}H and ^{13}C NMR data confirm that [9]aneS$_3$ is bound to the copper and reveal that CO is in fast exchange with the solvent. In the ^{1}H NMR spectrum of **2**, the singlet of the macrocycle (3.11 ppm) splits into an AA′BB′ pattern. This splitting pattern is consistent only with coordination of all three sulfur atoms to copper. In the ^{13}C NMR spectrum of the ^{13}CO isotopomer of **2**, a single, sharp ligand resonance is observed at 33.2 ppm. An additional, broad peak is observed in the carbonyl region at 178.7 ppm, indicative of rapid exchange of ^{13}CO at room temperature.

Complex **1** was similarly characterized. A Raman spectrum of **1** displays two prominent peaks at 1290 and 1550 cm^{-1}. The C$_2$D$_4$ isotopomer of **1** shows only one peak in the same region, at 1423 cm^{-1} (Figure 1b). Additional peaks appear in the C−D stretching region (2192, 2234, 2312, 2335 cm^{-1}) and at 973 and 781 cm^{-1}. Similar characteristics were noted by Hiraishi[9] in the Raman spectrum of Zeise's salt, K[PtCl$_3$(C$_2$H$_4$)]·H$_2$O, and the deuterated analogue. Hiraishi concluded that the two prominent modes observed between 1000 and 2000 cm^{-1} in metal−C$_2$H$_4$ compounds are coupled motions involving both C═C stretching and CH$_2$ scissoring motions. The two peaks in the Raman spectrum of **1** are accordingly assigned as coupled motions of C═C stretching and CH$_2$ scissoring. Substitution of C$_2$D$_4$ for C$_2$H$_4$ effectively decouples these motions; the vibrational frequencies in the C$_2$D$_4$ complex are then assigned to pure C═C stretching (higher energy) and CD$_2$ scissoring (lower energy). We assign the peak at 1423 cm^{-1} in the C$_2$D$_4$ isotopomer of **1** to the C═C stretch and those at 781 and 973 cm^{-1} to CD$_2$ scissoring motions. Calculations by density functional theory methods[10] corroborate motional coupling in **1** and loss of that coupling upon deuteration and are consistent with the above assignments. In the low-frequency region of the spectrum of **1**, a single, isotope-sensitive band was observed at 366 cm^{-1} (Figure 1b, inset). This mode is assigned as a metal−ethylene stretch. As in complex **2**, solid-state Raman and solution (acetone-d_6) ^{1}H NMR data for **1** are consistent with coordination of [9]aneS$_3$ to Cu(I) with an AA′BB′ multiplet at

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(7) All NMR spectra were taken on a Bruker AC300 spectrometer at room temperature in acetone-d_6.

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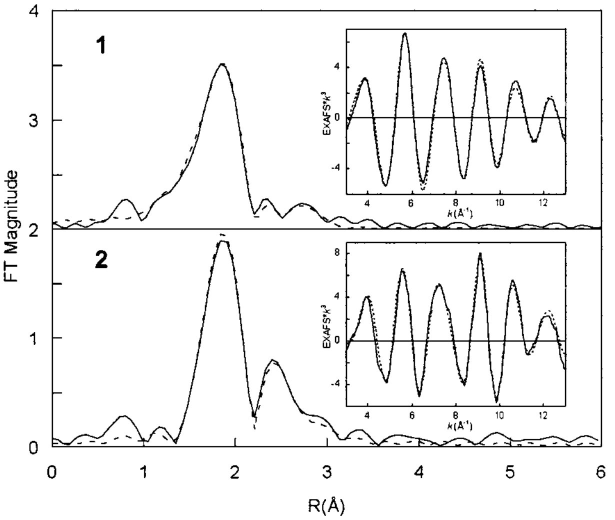

Figure 2. Non-phase-shift-corrected Fourier transforms (−) and fits to the data (- - -) for **1** (top) and **2** (bottom). Insets show the EXAFS signal (−) and fits to the data (- - -).

Table 1. Comparison of EXAFS Fit Results for **1** and **2**

compound	fit no.	CN	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)	error[a]
1	1	3 Cu−S	2.29	0.0042	−10.79	0.461
		6 Cu−C	3.17	0.0076		
	2	3 Cu−S	2.30	0.0036	−11.89	0.179
		6 Cu−C	3.17	0.0072		
		1 Cu−C	2.09	−0.0005		
	3	3 Cu−S	2.30	0.0042	−10.96	0.209
		6 Cu−C	3.18	0.0073		
		2 Cu−C	2.11	0.0029		
2	1	3 Cu−S	2.30	0.0030	−12.78	0.868
		6 Cu−C	3.13	0.0025		
	2	3 Cu−S	2.30	0.0030	−12.78	0.544
		6 Cu−C	3.14	0.0025		
		1 Cu−C	1.82	0.0012		
	3	3 Cu−S	2.31	0.0031	−12.40	0.361
		6 Cu−C	3.14	0.0085		
		1 Cu−C	1.83	0.0016		
		1 Cu−O[b]	3.02	0.0035		
			3.02	0.0035		

[a] Error is given by $\sum[(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2 k^6]/n$, where n is the number of data points. [b] These components represent the single-scattering path (top) and multiple-scattering path (bottom), which were linked during the refinement.

3.17 ppm in the ^{1}H NMR spectrum, attributable to the coordinated macrocycle. The only other peak in the ^{1}H NMR spectrum is that of free ethylene at 5.43 ppm. The low-frequency metal−ethylene vibration and the absence of bound ethylene in the solution ^{1}H NMR spectrum at room temperature suggest a weak metal−ethylene bond in **1**.

Cu K-edge EXAFS measurements were used to define the metrical parameters of **1** and **2**. For **1**, the Fourier transform (FT) of the EXAFS spectrum (Figure 2) is dominated by three Cu−S interactions at 2.30 Å, with a weakly resolved shoulder at low R corresponding to two Cu−C/N interactions at 2.11 Å. Inclusion of only one Cu−C/N interaction results in an unreasonably small Debye−Waller factor (Table 1). When no Cu−C/N interactions are included, a visually poor fit is obtained and a clear beat pattern remains in the residual. The outer shells of the FT are derived from the ~3.2 Å Cu−C/N interactions from the [9]aneS$_3$ ligand. The FT of the spectrum of **2** is also dominated by three Cu−S interactions at 2.31 Å. In addition, there is a weak Cu−C/N interaction at 1.83 Å. Strong evidence for a Cu(I)-bound CO is obtained from analysis of the outer-shell FT feature at ~2.4 Å (non-phase-shift-corrected), which is well fit by inclusion of multiple scattering interactions from a linear CO as well as by inclusion of Cu−C/N interactions from the [9]aneS$_3$ ligand (Table 1).

Table 2. CO Stretching Frequencies and Structural Data from Some Known Cu(I) Carbonyl Complexes

complex	ν(CO) (cm^{-1})	M−C[f] (Å)	ref
[Cu(en)(CO)]$^+$	2117	1.81	*a*
[Cu(HBpz$_3$)(CO)]$^+$	2083	1.76	*b*
[Cu(dien)(CO)]$^+$	2080	1.77	*c*
[{Cu(tmen)(CO)}$_2$Cl]$^{2+}$	2065	1.79	*d*
[(C$_5$H$_5$)Co{P(O)(OMe)$_2$}$_3$]Cu(CO)]$^+$	2078	1.76	*e*
complex **2**	2123	1.83	this work

[a] Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191. [b] Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051. [c] Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1978**, *17*, 1684. [d] Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1981**, *20*, 3382. [e] Klaüi, W.; Lenders, B.; Hessner, B.; Evertz, K. *Organometallics* **1988**, *7*, 1357. [f] All distances were determined by X-ray crystallographic analysis except those reported in this work.

Table 3. Stretching Frequencies and Structural Data from Some Known Cu(I) Ethylene Complexes

complex	ν(CC) + δ(CH$_2$) (cm^{-1})	M−C[e] (Å)	ref
[Cu(Bu$^t_2$P(NSiMe$_3$)$_2$)(C$_2$H$_4$)]$^+$	1516	1.987	*a*
[Cu(tmen)(C$_2$H$_4$)]$^+$	1525	1.969, 1.95	*b*
[Cu(bipy)(C$_2$H$_4$)]$^+$	1523	2.028, 2.019	*c, d*
[Cu(phen)(C$_2$H$_4$)]$^+$	1525	1.998, 2.022	*c, d*
complex **1**	1550	2.11	this work

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Given the solution lability and relative instability of **1** and **2**, solid-state methods have proven effective in their characterization. Characterization of **1** and **2** reveals weak metal−ethylene and metal−CO interactions. Comparison of structural and vibrational data for **1** and **2** with known copper(I)−ethylene and copper(I)−CO complexes (Tables 2 and 3) shows that **1** and **2** exhibit high ethylene and CO vibrational frequencies and long M−C bond distances. Room-temperature NMR data for **1** and **2** show that in these complexes the C$_2$H$_4$ and CO ligands are in competition with solvent. At room temperature, neither ethylene nor CO can displace CH$_3$CN from the starting material [Cu(CH$_3$CN)$_4$][PF$_6$] to form **1** or **2**. Together, these data suggest that the [9]aneS$_3$ complexes exhibit metal−ligand bonding interactions that are weaker than those of many known copper(I)−ethylene or copper(I)−CO species.

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