in the spectra obtained for this compound. Virtually all previous studies on coupled Cu(II) systems have employed only X-band measurements. We have observed[32] a similar diminution in the intensity of the $\Delta m = 2$ absorption on changing from X- to Q-band for the dimeric[33] complex $[Cu(adenine)_2(H_2O)]_2 \cdot 6H_2O$, though for that compound, in which the coupling is much stronger,[34] the $\Delta m = 2$ band can still be seen very weakly at Q-band with very high spectrometer gain settings. These observations emphasize the value of changing the applied microwave frequency in studying coupled copper(II) systems.

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Registry No. **1**, 91003-29-1; **2**, 91032-24-5; **3**, 83351-00-2; **4**, 83434-36-0; **5**, 83378-74-9; 1-MeUH, 615-77-0; *cis*-$(NH_3)_2Pt$(1-MeU)Cl, 85715-78-2.

Supplementary Material Available: Listings of atomic parameters, observed and calculated structure factors, and least-squares planes (Pt and Cu coordination planes, 1-MeU and 1-MeC planes) (13 pages). Ordering information is given on any current masthead page.

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Copper(I) Complexes with Unsaturated Small Molecules. Preparation and Structural Characterization of Copper(I)-Di-2-pyridylamine Complexes with Olefins, Acetylene, and Carbon Monoxide

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The syntheses, spectroscopy, and structures of Cu(I)-di-2-pyridylamine ($NH(py)_2$) complexes with ethylene, propylene, acetylene, and carbon monoxide ligands are presented. Complexes of the formulation $[Cu(NH(py)_2)(X)]Y$ ($X = C_2H_4$ and C_3H_6, $Y = ClO_4$; $X = C_2H_2$, $Y = BF_4$) and $[Cu(NH(py)_2)(CO)ClO_4]$ are characterized analytically and spectroscopically. The ethylene, acetylene, and carbonyl compounds are also characterized by X-ray diffraction techniques. The ethylene complex $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ crystallizes in the monoclinic space group $C2/c$ with 4 molecules per unit cell of dimensions $a = 9.829$ (1) Å, $b = 17.105$ (2) Å, $c = 8.672$ (1) Å, and $\beta = 93.806$ (1)° at −100 °C. Least-squares refinement of 116 variables led to a value of the conventional R index (on F) of 0.050 and of R_w of 0.049 for 1260 reflections having $F_o^2 > 2\sigma(F_o^2)$. The geometry about the Cu(I) ion, which is coordinated to two pyridyl nitrogen atoms and an ethylene molecule, is trigonal planar. The carbon-carbon bond distance of the coordinated ethylene molecule is 1.359 (7) Å. The acetylene complex $[Cu(NH(py)_2)(C_2H_2)]BF_4$ crystallizes in the monoclinic space group $C2/c$ with 4 molecules per unit cell of dimensions $a = 10.140$ (2) Å, $b = 17.782$ (4) Å, $c = 7.852$ (1) Å, and $\beta = 105.34$ (1)° at −100 °C. Least-squares refinement of 119 variables led to a value of the conventional R index of 0.046 and of R_w of 0.044 for 1259 independent reflections having $F_o^2 > 2\sigma(F_o^2)$. The coordination sphere about the Cu(I) ion is analogous to that found for the ethylene complex. The carbon-carbon bond distance of the coordinated acetylene molecule is 1.188 (11) Å. The carbonyl complex $[Cu(NH(py)_2)(CO)ClO_4]$ crystallizes in the triclinic space group $P\bar{1}$ with 2 molecules per unit cell of dimensions $a = 8.922$ (1) Å, $b = 10.755$ (1) Å, $c = 7.379$ (1) Å, $\alpha = 91.51$ (1)°, $\beta = 99.24$ (1)°, and $\gamma = 81.25$ (1)° at −100 °C. Least-squares refinement of 226 variables led to a value of the conventional R index of 0.028 and of R_w of 0.032 for 2774 independent reflections having $F_o^2 > 2\sigma(F_o^2)$. The Cu(I) ion is coordinated to two pyridyl nitrogen atoms and a carbonyl group in a trigonal-planar geometry. There is also a perchlorate oxygen atom at a distance of 2.429 (1) Å from the copper ion, which suggests a weak interaction between cation and anion. These complexes demonstrate that the copper coordination chemistry with ethylene, propylene, acetylene, and carbon monoxide is consistent with the proposed role of copper at the ethylene binding site of plants.

Recently we reported the synthesis, properties, and first structural characterization of two Cu(I)-ethylene complexes that are stable to loss of olefin, unlike the majority of previously reported cuprous-ethylene adducts.[1] Our interest in this area arises from the proposed role of copper in the binding of the plant hormone ethylene to its receptor site.[2,3] Although the identity of the binding site remains unknown, the properties of the native systems suggest the involvement of a metal ion. Of all the biologically important transition metals, only copper ion shows reactivity with ethylene and the ethylene analogues (propylene, acetylene, carbon monoxide) in an oxidation state commonly found in biological systems. However, the majority of Cu(I)-ethylene adducts are so unstable to loss of olefin that they have been in general only poorly characterized.[4-6] In contrast, the native systems show an apparent K_D for ethylene of $\sim 10^{-10}$ M.[7] It is thus impossible to determine whether or

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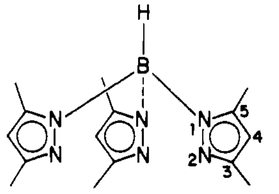
not the observed properties of the receptor site, especially the trends in activity of ethylene and ethylene analogues, are consistent with a binding site containing a cuprous ion. The compounds reported by us with the ligands hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $HB(3,5-Me_2(pz))_3$ (I), and hydrotris(1-pyrazolyl)borate, $HB(pz)_3$ (II), are indefinitely stable in the solid state under nitrogen and can be dissolved in olefin-free solvents without decomposition; hence, these compounds show binding of ethylene that is characteristic of the native systems. The structural characterization of these complexes revealed a relatively unperturbed carbon–carbon bond distance of the coordinated olefin (1.329 (9) and 1.347 (5) Å) compared with the free olefin value (1.337 (2) Å).[8,9] Although these relatively short bond lengths are not unique (values of 1.319–1.375 Å have been reported for a variety of transition metals[10]), a significant lengthening of this bond (1.41–1.46 Å) is usually observed on ethylene coordination to d^{10} metals such as those of the nickel triad.[9] These results suggest that σ bonding is the dominant interaction between metal and olefin; π back-bonding from metal ion to olefin is not of great importance. This type of bonding interaction can account at least in part for the observed trends in activity of ethylene analogues. Electron-withdrawing groups have been shown to decrease the activity of olefins in inducing the ethylene effect;[3] these groups enhance the π back-bonding from metal to olefin at the expense of the σ donation to the metal ion.



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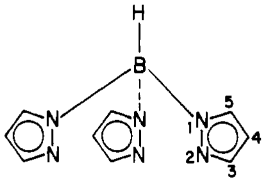

II

In this paper, we present the syntheses, spectroscopy, and structures of Cu(I)–di-2-pyridylamine complexes with ethylene, propylene, acetylene, and carbon monoxide ligands. The objective of this work is to determine whether or not the properties of the olefin complexes with I and II are general characteristics of Cu(I)–ethylene complexes with nitrogen donor ligands. In addition, we wished to establish that Cu(I) complexes with monoolefins, acetylene, and carbon monoxide exhibit the same type of structural chemistry. Our earlier report on Cu(I)–monoolefin complexes with I and II established the properties and types of structures of Cu(I)–ethylene complexes with nitrogenous ligands.[1] Cu(I)–carbonyl complexes have been extensively studied.[11] Indeed, the first well-characterized, stable Cu(I) complexes with ethylene[1] and carbon monoxide[11a,b] are those with I and II; thus, the structural chemistry of copper with these two small molecules is well established. However, we are unaware of any other examples of ethylene and acetylene forming structurally analogous Cu(I) complexes. Copper–acetylene chemistry is dominated by the formation of Cu(I)–acetylide complexes.[5,12] The Cu(I) complexes reported herein support the conclusions of our earlier work and demonstrate for the first time that ethylene and acetylene form isostructural complexes. A communication of the initial results on this Cu(I)–acetylene chemistry has appeared.[13]

Experimental Section

General Methods. All chemicals were reagent grade and were used as received unless otherwise noted. Tetrakis(acetonitrile)copper(I) tetrafluoroborate, $[Cu(CH_3CN)_4]BF_4$, was prepared according to a literature procedure.[14] The solvents methanol and diethyl ether were deaerated with prepurified nitrogen and stored over molecular sieves (4A), which were activated prior to use by heating at approximately 250 °C under high vacuum for several days and then stored under nitrogen. Standard glovebox and Schlenkware techniques were used in the handling of air-sensitive compounds. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283-B infrared spectrophotometer. NMR spectra were obtained in deuterioacetone with a Perkin-Elmer EM-390 spectrometer; all reported peak positions are relative to tetramethylsilane.

Preparations. (Ethylene)(di-2-pyridylamine)copper(I) Perchlorate, $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ (III). Copper perchlorate hexahydrate (0.25 g, 0.67 mmol) and copper dust (0.20 g, 3.1 mmol) were stirred in 10 mL of methanol overnight in an ethylene atmosphere. *Caution! The Cu(I)–ethylene adduct produced in this step is unstable and will explode if taken to dryness.*[15] The ligand di-2-pyridylamine, $NH(py)_2$, (0.23 g, 1.3 mmol) was added slowly as a powder. After completion of this addition, the reaction mixture was stirred for approximately 0.5 h and then filtered under nitrogen pressure. The volume of the filtrate was reduced with a stream of ethylene. A white, microcrystalline product was obtained on addition of diethyl ether. Anal. Calcd for $C_{12}H_{13}ClCuN_3O_4$: C, 39.79; H, 3.62; N, 11.60. Found: C, 39.74; H, 3.53; N, 11.44. IR (cm^{-1}): 3330 m, 3255 w, 3220 m, 3155 m, 3110 w, 3080 w, 3055 w, 1645 s, 1615 w, 1610 w, 1595 m, 1585 s, 1530 s, 1505 w, 1438 m, 1425 m, 1380 s, 1335 w, 1275 w, 1268 w, 1235 s, 1175 m, 1165 s, 1115 s, 1100 s, 1070 s, 1015 m, 955 w, 930 w, 912 m, 865 w, 840 w, 830 w, 815 w, 765 s, 735 w, 720 w, 650 w, 620 m. NMR (ppm): 9.90 (s, 1 H), 8.38 (d, 2 H), 8.03 (t, 2 H), 7.26 (q, 4 H), 4.70 (s, 4 H).

(Propylene)(di-2-pyridylamine)copper(I) Perchlorate, $[Cu(NH(py)_2)(C_3H_6)]ClO_4$ (IV). The procedure described above for the preparation of the ethylene complex III was used to prepare the analogous propylene complex IV. Anal. Calcd for $C_{13}H_{15}ClCuN_3O_4$: C, 41.50; H, 4.02; N, 11.17. Found: C, 41.44; H, 4.04; N, 11.10. IR (cm^{-1}): 3325 m, 3260 w, 3230 w, 3160 w, 3110 w, 3095 w, 3050 w, 1645 s, 1615 w, 1595 m, 1590 s, 1570 w, 1560 w, 1535 s, 1515 w, 1435 m, 1422 m, 1400 w, 1275 m, 1255 w, 1235 s, 1200 w, 1172 s, 1165 m, 1120 s, 1100 s, 1060 s, 1050 m, 1020 m, 1015 m, 955 w, 920 w, 915 m, 892 w, 878 m, 830 w, 788 m, 770 s, 735 w, 720 w, 705 w, 670 w, 655 w, 615 m. NMR (ppm): 9.86 (s, 1 H), 8.31 (d, 2 H), 7.95 (t, 2 H), 7.21 (q, 4 H), 5.48 (m, 1 H), 4.50 (m, 2 H), 1.81 (d, 3 H).

(Acetylene)(di-2-pyridylamine)copper(I) Tetrafluoroborate, $[Cu(NH(py)_2)(C_2H_2)]BF_4$ (V). Tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.40 g, 1.3 mmol) in approximately 10 mL of methanol was stirred under an acetylene atmosphere for approximately 1 h,

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Table I. Crystal Data for $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ (III), $[Cu(NH(py)_2)(C_2H_2)]BF_4$ (V), and $[Cu(NH(py)_2)(CO)ClO_4]$ (VI)

	III	V	VI
mol form	$C_{12}H_{13}ClCuN_3O_4$	$C_{12}H_{11}BCuF_4N_3$	$C_{11}H_9ClCuN_3O_5$
mol wt	364.26	347.59	362.20
a, Å	9.829 (1)	10.140 (2)	8.922 (1)
b, Å	17.105 (2)	17.782 (4)	10.755 (1)
c, Å	8.672 (1)	7.852 (1)	7.379 (1)
α, deg	90.0	90.0	91.51 (1)
β, deg	93.806 (1)	105.34 (1)	99.24 (1)
γ, deg	90.0	90.0	81.25 (1)
V, $Å^3$	1454.8 (6)	1365.3 (8)	690.7 (2)
Z	4	4	2
space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$
radiation (λ, Å)	Mo Kα (0.710 69) from graphite monochromator	Mo Kα (0.710 69) from graphite monochromator	Mo Kα (0.710 69) from graphite monochromator
2θ limits, deg	4–55	4–55	4–55
temp, °C	−100	−100	−100
abs coeff, cm^{-1}	17.61	17.07	18.60
transmissn factor	0.821–0.998	0.904–0.997	0.923–0.994
no. of unique data used ($F_o^2 > 2\sigma^2$))	1260	1259	2774
no. of variables	116	119	226
R	0.050	0.046	0.028
R_w	0.049	0.044	0.032

at which point the solution was dark red-brown in color. Di-2-pyridylamine (0.23 g, 1.3 mmol) was added slowly as a powder. The preparation was completed in the manner described above for the ethylene complex. Anal. Calcd for $C_{12}H_{11}BCuF_4N_3$: C, 41.47; H, 3.19; N, 12.09; Cu, 18.28. Found: C, 41.76; H, 3.46; N, 12.31; Cu, 18.62. IR (cm^{-1}): 3340 m, 3265 w, 3215 m, 3130 m, 3100 w, 3055 w, 1795 m, 1645 s, 1620 w, 1595 m, 1590 s, 1572 m, 1535 m, 1288 w, 1278 w, 1235 m, 1180 m, 1169 s, 1110 w, 1070 s, 1015 s, 912 m, 872 w, 832 w, 770 s, 718 m. NMR (ppm): 9.85 (s, 1 H), 8.48 (d, 2 H), 7.98 (t, 2 H), 7.26 (q, 4 H), 5.59 (s, 2 H).

(Perchlorato)carbonyl(di-2-pyridylamine)copper(I), $[Cu(NH(py)_2)(CO)ClO_4]$ (VI). The procedure described above for the preparation of the ethylene complex III was used to prepare the analogous carbonyl complex VI. Anal. Calcd for $C_{11}H_9ClCuN_3O_5$: C, 36.48; H, 2.50; N, 11.60. Found: C, 36.33; H, 2.55; N, 11.30. IR (cm^{-1}): 3335 m, 3250 w, 3215 w, 3150 w, 3120 w, 2110 s, 1642 s, 1615 w, 1592 m, 1585 s, 1558 w, 1530 s, 1432 m, 1420 m, 1275 w, 1235 m, 1170 m, 1165 m, 1115 s, 1100 s, 1070 s, 1040 s, 1015 m, 918 w, 910 m, 875 w, 865 w, 835 w, 765 s, 730 w, 720 w, 650 w, 620 m. NMR (ppm): 9.65 (s, 1 H), 8.50 (d, 2 H), 7.98 (t, 2 H), 7.23 (q, 4 H).

X-ray Data Collection and Structure Solution and Refinement. $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ (III). Crystals suitable for diffraction studies were obtained by vapor diffusion of diethyl ether into an ethylene-saturated methanol solution of III at room temperature. The crystal was handled in the manner described elsewhere[1] and was shown to be suitable for diffraction on the basis of ω scans, which showed the peak width at half-height to be ca. 0.25° at −100 °C. The cell parameters were then refined on the basis of 43 computer-centered reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I. Intensity data collection by the ω-scan technique, intensity measurement of standard reflections, empirical corrections for absorption, and data processing were performed as described elsewhere.[1] The solution and refinement of the structure were carried out using local modifications of programs supplied by the Enraf-Nonius Corp.[1,16] The copper atom was located by the heavy-atom Patterson method. The positions of the remaining non-hydrogen atoms were obtained by the usual combination of structure factor and Fourier synthesis calculations and full-matrix least-squares refinement. The function minimized in these refinements is given elsewhere.[1] Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[17] After convergence of the non-hydrogen portion of the molecule in which the atoms were refined anisotropically, the hydrogen atoms were located in a Fourier difference synthesis and refined satisfactorily. Least-squares refinement converged to $R = 0.050$ and $R_w = 0.049$ (R and R_w are defined elsewhere[1]). The relatively large R value results at least in part from the apparent disorder of the perchlorate group. The final difference map shows electron density (four peaks, 0.29–0.41 e/$Å^3$) close to the chlorine atom.

Table II. Final Atomic Coordinates (with Estimated Standard Deviations) for $[Cu(NH(py)_2)(C_2H_4)]ClO_4$ (III)

atom	*x*	*y*	*z*
Cu	0.000	0.14531 (3)	0.250
Cl	0.000	0.74004 (7)	0.250
O1	−0.0873 (3)	0.7871 (2)	0.3305 (3)
O2A	0.1124 (6)	0.7175 (4)	0.3961 (7)
O2B	0.0269 (8)	0.6756 (3)	0.3074 (7)
N1	−0.1262 (2)	0.0695 (1)	0.1477 (3)
N2	0.000	−0.0395 (2)	0.250
C11	−0.1062 (3)	−0.0082 (2)	0.1569 (3)
C12	−0.1922 (3)	−0.0609 (2)	0.0732 (4)
C13	−0.2994 (3)	−0.0330 (2)	−0.0183 (4)
C14	−0.3220 (3)	0.0471 (2)	−0.0266 (4)
C15	−0.2347 (3)	0.0957 (2)	0.0557 (4)
C1	−0.0634 (3)	0.2564 (2)	0.2142 (4)
H1	−0.077 (2)	0.262 (1)	0.100 (3)
H2	−0.136 (2)	0.259 (2)	0.276 (3)
HN	0.000	−0.085 (2)	0.250
H12	−0.173 (2)	−0.114 (1)	0.085 (3)
H13	−0.351 (3)	−0.067 (1)	−0.078 (3)
H14	−0.388 (3)	0.069 (1)	−0.094 (3)
H15	−0.250 (3)	0.155 (1)	0.053 (3)

The final positional parameters appear in Table II. General temperature factors appear in Table III.[18] Tables of the structure amplitudes (Table IV) and a complete listing of bond distances and angles (Table V) are available.[18]

$[Cu(NH(py)_2)(C_2H_2)]BF_4$ (V). Crystals suitable for diffraction studies were obtained by vapor diffusion of diethyl ether into an acetylene-saturated methanol solution of IV at room temperature. The crystal was handled in the manner described above. It was shown to be suitable for diffraction on the basis of ω scans, which showed the peak width at half-height to be 0.32° at −100 °C. The cell parameters were refined on the basis of 48 computer-centered reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I. Intensity data collection, intensity measurements of standard reflections, empirical corrections for absorption, and data processing were performed as described above.

All crystallographic calculations were performed on a Digital Equipment Corp. VAX 11/780 computer using a system of programs developed by Dr. J. C. Calabrese, Central Research and Development

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(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England; Vol. IV: (a) Table 2.2B; (b) Table 2.31.

(18) See paragraph at end of paper regarding supplementary material.

Table VI. Final Atomic Coordinates (with Estimated Standard Deviations) for $[\mathrm{Cu(NH(py)_2)(C_2H_2)]BF_4}$ (V)

atom	x	y	z
Cu	0.500	0.10218 (3)	0.250
F1	0.0193 (5)	0.1640 (2)	0.1187 (5)
F2	0.1056 (5)	0.2537 (3)	0.3191 (6)
N1	0.500	−0.0756 (3)	0.250
N2	0.3748 (3)	0.0287 (2)	0.3114 (4)
C1	0.4521 (6)	0.2079 (2)	0.2802 (7)
C2	0.3900 (4)	−0.0459 (2)	0.2998 (5)
C3	0.2955 (5)	−0.0972 (3)	0.3375 (5)
C4	0.1825 (5)	−0.0702 (3)	0.3856 (6)
C5	0.1668 (5)	0.0071 (3)	0.3956 (5)
C6	0.2620 (4)	0.0536 (3)	0.3597 (5)
B	0.000	0.2085 (4)	0.250
H1	0.383 (5)	0.222 (3)	0.330 (6)
H3	0.315 (5)	−0.140 (3)	0.330 (6)
H4	0.123 (5)	−0.104 (2)	0.416 (6)
H5	0.094 (5)	0.025 (3)	0.423 (6)
H6	0.249 (5)	0.104 (3)	0.367 (6)
H7	0.500	−0.114 (3)	0.250

Department, E. I. du Pont de Nemours and Co., Wilmington, DE. The copper atom was located by direct methods. The structure solution and refinement were performed as described above. Least-squares refinement converged to values of $R = 0.046$ and $R_w = 0.044$. All peaks in the final difference Fourier map are less than 0.55 e/Å^3, with the greatest density (0.2–0.55 e/Å^3) near the NH and $\mathrm{BF_4}$ groups.

The final positional parameters of the refined atoms appear in Table VI. General temperature factors appear in Table VII.[18] Tables of the structure amplitudes (Table VIII) and a complete listing of bond distances and angles (Table IX) are available.[18]

$[\mathrm{Cu(NH(py)_2)(CO)ClO_4}]$ (VI). Crystals suitable for diffraction studies were obtained by vapor diffusion of diethyl ether into a carbon monoxide saturated methanol solution of VI. The crystal chosen was handled in the manner described above. It was shown to be suitable for diffraction on the basis of ω scans, which showed the peak width at half-height to be 0.24° at −100 °C. The cell parameters were then refined on the basis of 50 computer-centered reflections chosen from diverse regions of reciprocal space. These parameters and other crystallographic data are summarized in Table I. Intensity data collection by the ω-scan technique, intensity measurement of standard reflections, empirical correction for absorption, and data processing were performed as described above.

The copper atom was located by direct methods. The structure solution and refinement were performed as described above. Least-squares refinement converged to values of $R = 0.028$ and $R_w = 0.032$. All peaks in the final difference Fourier map are less than 0.30 e/Å^3.

The final positional parameters appear in Table X. General temperature factors appear in Table XI.[18] Tables of the structure amplitudes (Table XII) and a complete listing of bond distances and angles (Table XIII) are available.[18]

Results

Synthesis and Properties. The syntheses of the Cu(I)–di-2-pyridylamine complexes with ethylene, propylene, acetylene, and carbon monoxide are straightforward and are presented in eq 1–3. The preparations of III, IV, and VI take advantage of the well-established reduction of Cu(II) salts by copper metal in the presence of olefins and carbon monoxide.[14,15] The product of this first step is presumably a Cu(I) adduct of the small molecule, but these complexes were not isolated because of the tendency of these materials to explode when dry;[15] rather, the ligand $\mathrm{NH(py)_2}$ was added slowly as a powder. The compounds with the indicated stoichiometries were isolated upon addition of diethyl ether. The acetylene complex V was prepared by the procedure shown in eq 2 to minimize the explosion hazards of mixing acetylene with copper-containing materials.[4a] Addition of acetylene to a methanol solution of $[\mathrm{Cu(CH_3CN)_4]BF_4}$ produced a deep red solution, to which the ligand was added slowly as a powder. Filtration of the material yielded a light yellow filtrate. Concentration with acetylene and addition of diethyl ether yielded V.

$$\mathrm{Cu(ClO_4)_2{\cdot}6H_2O + Cu \xrightarrow[X]{methanol} \xrightarrow{NH(py)_2} [Cu(NH(py)_2)(X)]ClO_4} \quad (1)$$

III, X = ethylene
IV, X = propylene

$$\mathrm{[Cu(CH_3CN)_4]BF_4 + C_2H_2 \xrightarrow{methanol} \xrightarrow{NH(py)_2} \underset{V}{[Cu(NH(py)_2)(C_2H_2)]BF_4}} \quad (2)$$

$$\mathrm{Cu(ClO_4)_2{\cdot}6H_2O + Cu \xrightarrow[methanol]{CO} \xrightarrow{NH(py)_2} \underset{VI}{[Cu(NH(py)_2)(CO)ClO_4]}} \quad (3)$$

Table X. Final Atomic Coordinates (with Estimated Standard Deviations) for $[\mathrm{Cu(NH(py)_2)(CO)ClO_4}]$ (VI)

atom	x	y	z
Cu	0.08300 (3)	0.24005 (2)	0.25356 (3)
Cl	0.24379 (5)	0.30681 (4)	−0.30022 (7)
O1	0.2244 (2)	0.2078 (1)	−0.4373 (2)
O2	0.2788 (2)	0.2454 (2)	−0.1258 (2)
O3	0.1037 (2)	0.3925 (1)	−0.3114 (3)
O4	0.3650 (2)	0.3696 (2)	−0.3329 (3)
O5	0.1961 (2)	0.4707 (2)	0.1706 (3)
N1	−0.1215 (2)	0.2188 (1)	0.3111 (2)
N2	0.1493 (2)	0.0580 (1)	0.2062 (2)
N3	−0.0795 (2)	−0.0031 (1)	0.2769 (2)
C1	0.1526 (3)	0.3816 (2)	0.1987 (3)
C11	−0.1716 (2)	0.1080 (2)	0.3135 (3)
C12	−0.3181 (2)	0.0979 (2)	0.3525 (3)
C13	−0.4139 (2)	0.2043 (2)	0.3881 (3)
C14	−0.3636 (2)	0.3206 (2)	0.3844 (3)
C15	−0.2197 (2)	0.3237 (2)	0.3463 (3)
C21	0.0649 (2)	−0.0322 (2)	0.2278 (3)
C22	0.1187 (2)	−0.1606 (2)	0.2012 (3)
C23	0.2624 (2)	−0.1947 (2)	0.1555 (3)
C24	0.3509 (2)	−0.1022 (2)	0.1333 (3)
C25	0.2907 (2)	0.0203 (2)	0.1588 (3)
HN	−0.116 (2)	−0.056 (2)	0.288 (3)
H12	−0.345 (2)	0.021 (2)	0.360 (3)
H13	−0.506 (2)	0.199 (2)	0.408 (3)
H14	−0.427 (3)	0.397 (2)	0.401 (3)
H15	−0.184 (3)	0.403 (2)	0.340 (3)
H22	0.062 (2)	−0.214 (2)	0.213 (3)
H23	0.299 (3)	−0.277 (2)	0.143 (3)
H24	0.453 (2)	−0.122 (2)	0.102 (3)
H25	0.341 (2)	0.077 (2)	0.139 (3)

The procedures outlined in eq 1–3 allow the preparation of white, crystalline compounds whose analytical, physical, and spectroscopic properties are consistent with the indicated formulations. All of these complexes react in solution with the ambient atmosphere to produce Cu(II) products that are currently being characterized. As with the other Cu(I)–monoolefin complexes recently reported by us,[1] these compounds give excellent analytical results without storage of the compounds in the presence of olefin, acetylene, or carbon monoxide. Crystalline compounds appear to be indefinitely stable in a nitrogen atmosphere and can be dissolved in deaerated solvents without significant decomposition, as indicated by the lack of decomposition products in the NMR spectra. The proton resonances for the coordinated small molecules can be assigned easily, as the NMR spectra are rather simple, and fall in the range observed both for Cu(I) complexes and for the other d^{10} metal complexes. Infrared spectra of these compounds also support the indicated formulations for III–VI. Although it is difficult to assign olefinic stretching frequencies unambiguously, there are bands at 1505 and 1515 cm^{-1} that we assign tentatively to the C=C stretching frequencies of the coordinated ethylene and propylene molecules, respectively, on the basis of the absence of bands in this region for the analogous acetylene and carbonyl

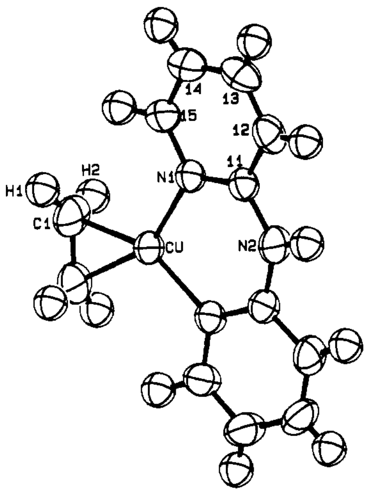

Figure 1. View of the [Cu(NH(py)$_2$)(C$_2$H$_4$)] cation (III). The vibrational ellipsoids are drawn at the 50% level in this and subsequent figures. Atom labels are included.

compounds V and VI.[9a] The infrared spectrum of the acetylene complex has a weak band at 1795 cm^{-1} that can be assigned to the C≡C stretching frequency of the coordinated acetylene molecule. This value is 179 cm^{-1} lower than that observed for free acetylene (1974 cm^{-1}).[19] Similarly, the CO complex VI has a strong band at 2110 cm^{-1} that can be assigned to a carbonyl stretching frequency. This value is somewhat higher than that typically observed for Cu(I)–CO complexes (2005–2080 cm^{-1}),[11] although it is not unique.[11d] In addition, the perchlorate band is split, which suggests unidentate coordination of the ClO_4^- group (vide infra).

Descriptions of the Structures. [Cu(NH(py)$_2$)(C$_2$H$_4$)]ClO$_4$. The overall structure of III is apparent in the drawing of the molecule (Figure 1) and consists of a three-coordinate Cu(I) cation and a well-separated perchlorate anion; the shortest Cu–O distance is 3.85 Å. The complex has twofold symmetry in the crystal. The copper atom is coordinated to two pyridine nitrogen atoms and an ethylene molecule in a trigonal-planar arrangement. The atoms Cu, C1, C1′, N1, and N1′ are essentially coplanar. The bond angles around the copper atom sum to 360°. The dihedral angle between the planes defined by Cu, C1, and C1′ and Cu, N1, and N1′ is 9.7°.

Selected bond distances and angles are presented in Table XIV. There are no unusual features in the copper coordination sphere. The observed Cu–N bond lengths are typical of three-coordinate Cu(I) complexes (1.93–2.16 Å).[1,20] Similarly, the Cu–C1 bond distance falls in the range observed previously.[1] The carbon–carbon bond distance of the coordinated ethylene molecule (1.359 (7) Å) is only slightly larger than or essentially unchanged from the value for the free molecule (1.337 (2) Å)[8,9] and the values for Cu(I)–C$_2$H$_4$ complexes previously reported (1.329 (9) and 1.347 (5) Å).[1] This distance is considerably shorter than the values observed for other d^{10} metal–olefin complexes (1.41–1.46 Å).[9]

[Cu(NH(py)$_2$)(C$_2$H$_2$)]BF$_4$. The overall structure of IV is apparent in the drawing of the molecule (Figure 2) and consists of a three-coordinate Cu(I) cation and a well-separated tetrafluoroborate anion; the shortest Cu–F distance is 4.839 (2) Å. The complex has twofold symmetry in the crystal. The copper atom is coordinated to two pyridine nitrogen atoms and a side-bound acetylene molecule. The overall structure is essentially the same as that for the ethylene cation. The entire molecular complex is close to planar. The bond angles around the copper atom sum to 360°. The dihedral angle between the planes defined by Cu, C1, and C1′ and Cu, N$_2$, and N$_2$′ is 5.1°.

Table XIV. Selected Bond Distances (Å) and Angles (deg) for [Cu(NH(py)$_2$)(C$_2$H$_4$)]ClO$_4$, [Cu(NH(py)$_2$)(C$_2$H$_2$)]BF$_4$, and [Cu(NH(py)$_2$)(CO)ClO$_4$]

	[Cu(NH(py)$_2$)(C$_2$H$_4$)]ClO$_4$		
Cu–C1	2.019 (3)	C12–C13	1.362 (5)
Cu–N1	1.963 (2)	C13–C14	1.388 (5)
N1–C11	1.345 (3)	C14–C15	1.368 (4)
C11–N2	1.388 (3)	C15–N1	1.367 (3)
C11–C12	1.399 (4)	C1–C1′	1.359 (7)
C1–Cu–C1′	39.3 (2)	C11–C12–C13	119.2 (3)
C1–Cu–N1	111.9 (1)	C12–C13–C14	119.6 (3)
N1–Cu–N1′	97.3 (1)	C13–C14–C15	118.8 (3)
N1–C11–N2	120.7 (3)	C14–C15–N1	122.8 (3)
N1–C11–C12	122.0 (3)	C11–N2–C11′	134.8 (3)
	[Cu(NH(py)$_2$)(C$_2$H$_2$)]BF$_4$		
Cu–N2	1.968 (3)	B–F1	1.354 (5)
Cu–C1	1.971 (4)	B–F2	1.334 (4)
C1–C1′	1.188 (11)		
N2–Cu–N2′	96.8 (2)	F1–B–F1′	108.5 (5)
N2–Cu–C1	114.1 (2)	F1–B–F2	113.5 (3)
C1–Cu–C1′	35.1 (3)	F1–B–F2′	107.7 (3)
C1′–C1–H1	164 (3)	F2–B–F2′	105.9 (7)
H1–C1–Cu	124 (3)		
	[Cu(NH(py)$_2$)(CO)ClO$_4$]		
Cu–N1	1.985 (1)	Cu–C1	1.808 (2)
Cu–N2	1.996 (1)	Cu–O1	2.429 (1)
N1–Cu–C1	129.4 (6)	N2–Cu–C1	132.8 (6)
N1–Cu–N2	95.52 (5)	N2–Cu–O1	87.77 (4)
N1–Cu–O1	97.18 (5)	O1–Cu–C1	98.49 (7)

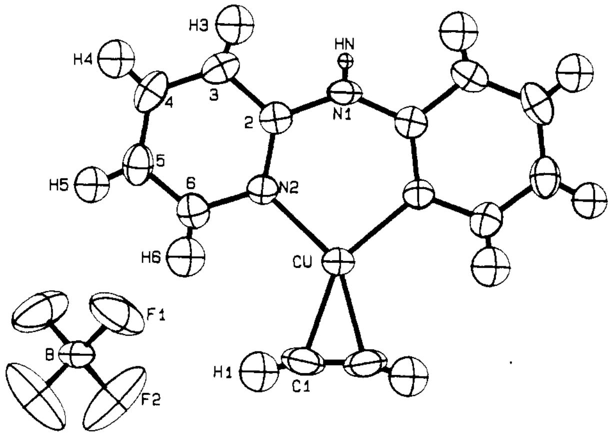

Figure 2. View of [Cu(NH(py)$_2$)(C$_2$H$_2$)]BF$_4$ (V).

Selected bond distances and angles are presented in Table XIV. The observed bond distances and angles for the ligand NH(py)$_2$ are nearly identical with those determined in the structure of III and are, therefore, not tabulated here (Table IX). The Cu–N and Cu–C contacts are the same in both structures. The carbon–carbon length of the bound C$_2$H$_2$ group (1.188 (11) Å) is essentially the same as that for the free molecule (1.204 Å).[21]

[Cu(NH(py)$_2$)(CO)ClO$_4$]. The overall structure of VI is apparent in the drawing of the molecule (Figure 3). The Cu(I) ion is coordinated to two pyridine nitrogen atoms from NH(py)$_2$ and a carbonyl group in a trigonal-planar arrangement. In addition, an oxygen atom from the perchlorate anion

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[19] Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 387.

[20] (a) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1–95. (b) Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883–1887. (c) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Ibid.* **1982**, *21*, 3250–3252. (d) Karlin, K. D.; Gultneh, Y.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1982**, *104*, 5240–5242.

[21] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 230.

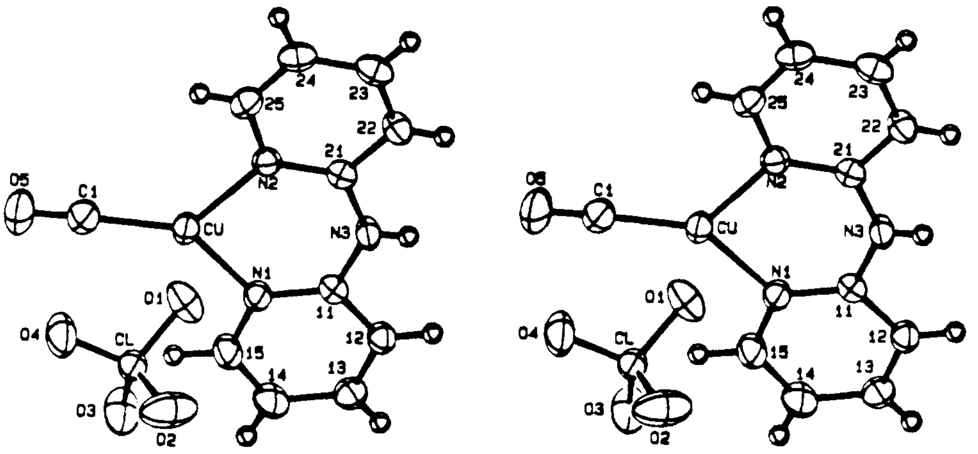

Figure 3. Stereoview of [Cu(NH(py)$_2$)(CO)ClO$_4$] (VI).

is found at a distance of 2.429 (1) Å from the copper atom. This distance is significantly longer than typical Cu(I)–O bond lengths (1.84–2.23 Å)[20b,22] but too close to ignore in light of the effect of this interaction on the infrared properties of this complex. Hence, the molecule can be described as a trigonal-planar Cu(I) cation with a weakly coordinated ClO$_4$ anion. The bond angles around the copper atom sum to nearly 360°. This weak association of an anion has been observed with other Cu(I) complexes having three other ligands at normal distances (vide infra).[11d,23]

Selected bond distances and angles are presented in Table XIV. The observed bond distances and angles for the NH(py)$_2$ ligand are nearly identical with those determined in the structure of III (Table XIV) and are therefore not tabulated here (Table XIII[18]). The Cu–N contacts are somewhat longer than those observed in the C_2H_2 analogue but fall in the range observed for three-coordinate Cu(I) complexes. The N–Cu–N bond angle is essentially the same as those determined for III and V. The Cu–C1 distance (1.808 (2) Å) is somewhat longer than that typically observed in Cu(I)–carbonyl complexes[11] but the same as that (1.806 (6) Å) observed for [Cu(en)(CO)BPh$_4$] (en = ethylenediamine, BPh$_4$ = tetraphenylborate) in which there is a close association between the trigonal-planar Cu(I) cation and a phenyl group of the BPh$_4$ anion.[11d]

Discussion

The objective of the present study was to determine whether or not the properties of the Cu(I)–ethylene complexes previously reported by us are characteristic of Cu(I)–monoolefin complexes in general.[1] Because this previous study with ligands I and II suggested that the trigonal-planar geometry was the preferred geometry for monoolefin complexes, the ligand di-2-pyridylamine, NH(py)$_2$, was used to generate three-coordinate Cu(I) complexes with monoolefins, acetylene, and carbon monoxide. A number of other bidentate nitrogen-donating ligands were tried unsuccessfully in the preparation shown in eq 1: dihydrobis(3,5-dimethyl-1-pyrazolyl)borate, dihydrobis(1-pyrazolyl)borate, and bis(2-imidazolyl)methane.[24] The preparations with NH(py)$_2$ yield complexes that are stable to loss of olefin, acetylene, or carbon monoxide in an inert atmosphere and that have been characterized analytically, spectroscopically, and structurally (for III, V, and VI). The infrared data were useful in formulating structures for these complexes and suggested that the olefin and acetylene complexes were somewhat different from the carbonyl complex, which appeared to have a coordinated perchlorate. This anion–cation interaction was confirmed in the structural study of VI (Figure 3). In addition, the relatively small shift (179 cm^{-1}) of the carbon–carbon stretching frequency of the coordinated acetylene molecule of V from the free-molecule value suggested that the bonding interaction between the Cu(I) ion and acetylene might be different from that typically observed for d^{10} metal–acetylene complexes and in accord with the bonding scheme presented in our previous study.[1] Shifts of this stretching frequency of 500 cm^{-1} or more are typical for complexes with other metal ions and are attributed to the π back-bonding interaction from metal ion to acetylene.[19]

The structural studies of III and V confirm and extend the conclusions from our earlier study of Cu(I)–monoolefin complexes.[1] As shown in Figure 1, the ethylene complex forms a trigonal-planar complex, with the ethylene molecule in the plane defined by the copper atom and the pyridyl nitrogen atoms; the perchlorate anion is well separated from the cation. This result is consistent with the observation that the trigonal-planar geometry is the dominant structural type for Cu(I)–monoolefin complexes, although tetrahedral complexes can be obtained with the proper choice of ligands. The acetylene complex V (Figure 2) has the same overall structure; indeed, the copper coordination spheres in the two compounds are nearly identical in terms of Cu–N and Cu–C bond distances and angles. This similarity of features between ethylene and acetylene complexes is typical of d^{10} transition metals,[9] but this study represents the first demonstration of an analogous chemistry for Cu(I) complexes. Cu(I)–acetylene chemistry is dominated by the formation of Cu(I)–acetylide complexes.[4a,5,12] These complexes have been extensively characterized and generally have an oligomeric structure with both σ bonding to a carbon atom and π bonding to the acetylenic bonds. Although the intense red color of the initial mixture of Cu(I) ion and acetylene (eq 2) suggests formation of at least some Cu(I)–acetylide complex, the only isolated product was V.

A second feature of the ethylene and acetylene complexes reported here that is in accord with our previous work is the effect of coordination to cuprous ion on the carbon–carbon bond of the bound molecule. For the ethylene complex II, the olefinic bond is only slightly longer than the value for free ethylene (1.337 (2) Å)[21] and close to the values determined for the coordinated ethylene molecule in the complexes with I and II (1.329 (9) and 1.347 (5) Å, respectively).[1] Similarly, the carbon–carbon bond distance of the coordinated acetylene molecule (1.188 (11) Å) is also essentially unchanged from that of the free molecule (1.204 Å).[21] Similar results have

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(22) (a) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 140–146. (b) Gagne, R. R.; Kreh, R. P.; Dodge, J. *J. Am. Chem. Soc.* **1979**, *101*, 6917–6927. (c) Messmer, G. G.; Palenik, G. J. *Inorg. Chem.* **1969**, *8*, 2750–2754.

(23) Gaughan, A. P.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657–1667.

(24) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294. (b) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99–109. (c) Joseph, M.; Leigh, T.; Swain, M. L. *Synthesis* **1977**, 459–461.

been obtained with other noncyclic monoolefins[1,6a] and disubstituted acetylenes.[25] These results are in accord with the bonding scheme suggested above.

The copper coordination sphere of the carbonyl complex VI (Figure 3) is different from that of the ethylene and acetylene complexes described above in that the perchlorate anion is clearly associated with the Cu(I) cation. The geometry about the copper atom can be described as trigonal planar with a weakly coordinated perchlorate group in the axial position. The Cu–O distance is too great to be considered typical of copper(I) complexes, but also too close to ignore, especially in light of the splitting of the perchlorate band in the infrared spectrum. This type of interaction has been observed with other Cu(I) complexes and with a Cu(I)–carbonyl complex in particular, [Cu(en)(CO)BPh$_4$] (VII), where en = ethylenediamine and BPh$_4$ = tetraphenylborate.[11d] In the latter complex, one of the phenyl groups from the BPh$_4$ moiety is found at a rather long distance (Cu–C distances of 2.71–2.92 Å) above the essentially trigonal-planar cuprous ion; thus, the geometry is essentially the same as that in VI. The carbonyl stretching frequencies for the two compounds are nearly identical (2110 cm^{-1} for VI and 2117 cm^{-1} for VII). The structural chemistry of Cu(I)–carbonyl complexes is similar to that for the isoelectronic Ni(0)–carbonyl compounds, in which the nickel atom is generally four-coordinate.[26] There is a strong similarity in the structural chemistry of olefin complexes as well.[1] A significant difference, however, between the copper and nickel systems is the manner in which the metal attains the desired coordination number. Ni(0) complexes with two or more carbonyl groups are well-known. However, cuprous ion does not appear to coordinate more than one carbonyl. Crystals of VI were grown in the presence of a large excess of carbon monoxide; however, the fourth position is occupied by the perchlorate group rather than an additional carbonyl group. There is also a report in the literature of a two-coordinate Cu(I) complex that will react with carbon monoxide only in the presence of an additional ligand such as *N*-methylimidazole to generate a four-coordinate carbonyl complex.[27] These results may be a manifestation of the poor back-bonding ability of the cuprous ion.

Conclusion

This work demonstrates that the coordination chemistry of copper complexes with ethylene, propylene, acetylene, and carbon monoxide is consistent with the proposed role of copper in the ethylene effect of plants.[2] With the proper choice of ligands, stable (to loss of small molecule) complexes can be prepared and fully characterized. The monoolefin compounds exhibit the same physical and spectroscopic properties and structures as the compounds previously reported by us.[1] The lack of a significant effect on the length of the coordinated olefinic bond appears to be a general property of Cu(I) complexes with noncyclic monoolefins and suggests that σ bonding between cuprous ion and the coordinated olefin is the dominant bonding interaction. This type of bonding has important biological implications as it would account at least in part for the observed decrease in biological activity relative to ethylene for olefins with electron-withdrawing groups,[1-3] which would enhance the back-bonding interaction from metal to olefin but weaken the σ donation from olefin to the metal ion. This type of bonding interaction appears to be important in the bonding of acetylene as well, as coordination to cuprous ion has no effect upon the coordinated acetylenic bond. This study represents the first demonstration of ethylene and acetylene forming isostructural Cu(I) complexes. If copper is indeed at the ethylene binding site, then cuprous ion should form stable complexes with all of the biologically active olefins and acetylenes, as well as carbon monoxide. There are now well-characterized Cu(I) complexes with all three of these types of unsaturated small molecules. Although the identity of the ethylene receptor site remains unknown, the copper coordination chemistry with ethylene and ethylene analogues supports the suggestion of a copper ion as an ethylene binding site in plant tissue.

Acknowledgment. The technical assistance of R. M. Swiatek, C. W. Dietrich, and L. Lardear is gratefully acknowledged. Helpful discussions with Drs. D. L. Thorn, T. H. Tulip, and P. L. Watson are greatly appreciated.

Registry No. III, 91128-06-2; IV, 91128-08-4; V, 91128-09-5; VI, 91128-10-8; [Cu(CH$_3$CN)$_4$]BF$_4$, 15418-29-8; copper perchlorate, 13770-18-8.

Supplementary Material Available: Listings of general temperature factors (Tables III, VII, and XI), structure amplitudes (Tables IV, VIII, and XII), and distances and angles (Tables V, IX, and XIII) (60 pages). Ordering information is given on any current masthead page.

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