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Cobalt(II) and Nickel(II) Complexes of Methyldiphenyl-4-pyridylphosphonium Bromide. Effects of a Cationic Pyridyl Ligand

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In recent years there has been considerable interest in pseudotetrahedral zwitterionic complexes formed between cationic ligands and transition metal halides (eq 1).[1-4] In the

$$L^+X^- + MX_2 \rightarrow [M(L^+)X_3^-] \qquad (1)$$

cases studied the effect of the cationic site has evidently not been effectively transmitted to the ligand donor atom.[1] Despite decreasing ligand basicity, the electronic behavior of these ligands in transition metal complexes appears similar to the analogous neutral ligands. This paper reports the preparation and characterization of the bromide salts of two new cationic ligands, the methyldiphenyl-4-pyridylphosphonium cation (P+py) and the methyldiphenyl-4-picolylphosphonium cation (P+pic), along with their complexes with cobalt(II) and
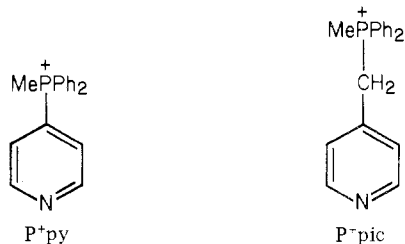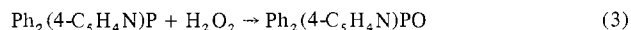

nickel(II) bromides. These are the first reported cationic ligands in which the donor atom is part of an aromatic ring, and in the case of P+py the cationic phosphonium site is attached right to the ring, where its effect could be transmitted to the donor site directly through the π system of the ring. We hoped therefore that the cationic site could have a greater influence on the donor site than had been previously observed.

Results

Diphenyl-4-pyridylphosphine was prepared by the reaction of 4-pyridyllithium with chlorodiphenylphosphine

$$Ph_2PCl + 4\text{-}LiC_5H_4N \rightarrow Ph_2(4\text{-}C_5H_4N)P \qquad (2)$$
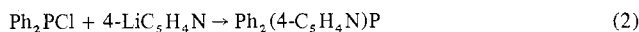
Diphenyl-4-pyridylphosphine could be characterized by oxidation to the monoxide with 30% hydrogen peroxide and to the dioxide with m-chloroperbenzoic acid in chloroform

$$Ph_2(4\text{-}C_5H_4N)P + H_2O_2 \rightarrow Ph_2(4\text{-}C_5H_4N)PO \qquad (3)$$

$$Ph_2(4\text{-}C_5H_4N)P + m\text{-}ClC_6H_4CO_3H \rightarrow Ph_2(4\text{-}C_5H_4NO)PO \qquad (4)$$

The bromide salts of P+py and P+pic were then prepared as shown in eq 5 and 6.

The Co(II) and Ni(II) complexes form blue crystals not apparently sensitive to atmospheric moisture. The room-temperature magnetic moments, μ_{eff}, for the Co(II) complexes (Table I) fall within the 4.4–4.8-BM range expected for tetrahedral or pseudotetrahedral Co(II) complexes.[5] The room-temperature μ_{eff} values for the Ni(II) complexes (Table I) are in the range 3.6–4.0 BM expected for tetrahedral Ni(II)

Table I. Magnetic Moments[a] and Molar Conductance[b] Values

Complex	Molar conductance, cm^2 ohm^{-1} mol^{-1}	μ_{eff}, BM[c]
Et$_4$N$^+$[Co(C$_5$H$_5$N)Br$_3$]$^-$	95 (CH$_3$CN)	4.65
	75 (CH$_3$NO$_2$)	
Co(P$^+$py)Br$_3$	84 (CH$_3$CN)	4.74
Co(P$^+$pic)Br$_3$	65 (CH$_3$CN)	4.70
	24 (CH$_3$NO$_2$)	
Ni(P$^+$py)Br$_3$	56 (CH$_3$NO$_2$)	3.80
Ni(P$^+$pic)Br$_3$	57 (CH$_3$NO$_2$)	3.70

[a] Values obtained at room temperature with a Faraday balance (HgCo(NCS)$_4$ calibration); corrected for the diamagnetic contribution of the ligands. [b] Values obtained on approximately 10^{-3} M solutions in the designated solvents. [c] Values obtained to within ±0.05 BM.
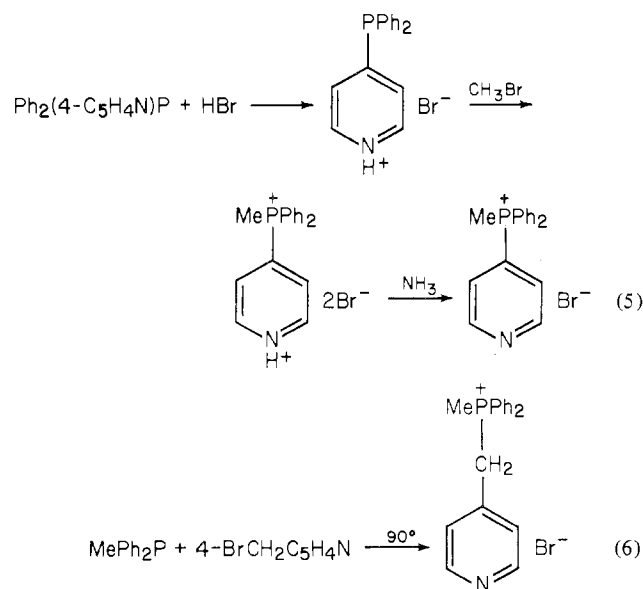
complexes.[6] Typical C_{3v} complexes of nickel bromide have values about 0.1–0.2 BM lower.[2,7]

The molar conductance values (Table I) in nitromethane or acetonitrile suggest that extensive solvolysis of these complexes is taking place in solution to give ionic species. The electronic spectra (visible region) of acetonitrile solutions of the complexes showed noticeable shifts from the spectra obtained on solid samples, indicating different species in the solid state and in solution (vide infra).[2,3,7]

The electronic spectra of the Co(II) complexes are characteristic of pseudotetrahedral symmetry.[8,9] The bands observed at 4700 and 7500 cm^{-1} (Table II) are assigned to components of the ν_2 transition in tetrahedral complexes (transitions to the $^4A_2$ and ^4E components of the $^4T_1(F)$ state).[8,9] The absorption maxima found at 14,500 and 15,000 cm^{-1} (Table II) are attributed to the two components of the ν_3 transition ($^4T_1(P)$ state) in tetrahedral complexes. A shoulder at 16,000 cm^{-1} is attributed to a transition to a doublet state.[10] The band at 8800 cm^{-1} in the observed spectra of the Ni(II) complexes (Table II) is assigned to the higher energy component of the ν_2 transition in tetrahedral Ni(II) complexes, and the asymmetric band at 15,500 cm^{-1} is then composed of the unresolved components of the ν_3 transition.[8,9]

Discussion

The higher absorption energies listed for the P+py complexes compared to the others (Table II) indicate a slightly higher

Table II. Electronic Spectral Data[a]

Complex	Absorption maxima,[b] cm^{-1}
Co(P$^+$py)Br$_3$	4720 w, 7520, 14,700, 15,300 sh, 16,100 sh
Co(P$^+$pic)Br$_3$	4720 w, 7400, 14,550, 15,200 sh, 16,200 sh
Et$_4$N$^+$[Co(C$_5$H$_5$N)Br$_3$]$^-$	4720 w, 7250, 14,600, 15,300 sh, 16,200 sh
Ni(P$^+$py)Br$_3$	8850 w, 15,500
Ni(P$^+$pic)Br$_3$	8770 w, 15,400

[a] Obtained with a Cary Model 14 spectrophotometer on Nujol mulls spread on filter paper. [b] Key: w, weak; sh, shoulder.

ligand field for P$^+$py. The absolute values obtained for Dq (Table III) are not too significant but the trend, though small, appears to be real. This is supported by the trend in Δ (Table III), which is related to the difference in ligand field strength between the pyridyl ligand and the bromides,[8] and is thus expected to increase with the increasing field strength of the pyridyl ligand. (The Dq values fall between 285 cm^{-1} found[11] for CoBr$_4$$^{2-}$ and 445 cm^{-1} found for Co(C$_5$H$_5$N)$_2$Br$_2$,[10] in accordance with the average ligand field approximation.[11])

As shown in the previous studies, the cationic site has no large effect on the electronic behavior of the ligands. The slightly higher field for P$^+$py presumably indicates some increase in the π-acceptor nature of the pyridyl ring.[4]

An absorption is noted in the 28,000-cm^{-1} region of the spectrum[12] of Co(P$^+$py)Br$_3$, which is missing in the spectra[12] of Co(P$^+$pic)Br$_3$ and Et$_4$N$^+$[Co(C$_5$H$_5$N)Br$_3$]$^-$. This absorption disappeared in the solution spectrum (CH$_3$CN), and since conductivity measurements indicated dissociation in solution, it seems likely that the removal of the P$^+$py ligand is responsible for the loss of absorption. Thus, since this region is often associated with charge-transfer transitions from the metal to ligand π-acceptor orbitals,[13] evidence points to a Co(II) → P$^+$py transition. The corresponding transition in Co(II) complexes with poorer π-acceptor ligands would be found at higher energies and therefore obscured by the Br → Co(II) transitions[13] found at 34,000–37,000 cm^{-1}.

Experimental Section

Materials. 4-Bromopyridine was obtained by adding aqueous KOH to a chilled aqueous solution of 4-bromopyridine hydrochloride and extracting the product with ether. The 4-bromopyridine could be obtained by removing the ether just before use. 4-(Bromomethyl)pyridine was obtained from its hydrobromide by the same procedure. 4-(Bromomethyl)pyridine hydrobromide was prepared from 4-pyridinemethanol and HBr.[14] The Et$_4$N$^+$[Co(C$_5$H$_5$N)Br$_3$]$^-$ was prepared according to the procedure of Sharp.[15]

Diphenyl-4-pyridylphosphine. To 49 ml of an 0.85 M solution of n-butyllithium (0.0415 mol) in dry ether at −78° was added dropwise 5.6 g of 4-bromopyridine (0.0355 mol) in 40 ml of ether. The resulting suspension of 4-pyridyllithium was stirred for 10–15 min at −78°, and 8.5 g of chlorodiphenylphosphine (0.0385 mol) in 35 ml of ether was then added. The reaction mixture was allowed to warm to room temperature and was then poured into 8 ml of NH$_3$ mixed with 50 g of ice. The organic layer was separated, washed twice with water, and dried. After the ether was removed, the residual material was distilled without a column, and the material which distilled at 135–185° (0.1 mm) was collected. It solidified upon cooling, and the solid was crystallized twice from hexane (under a nitrogen atmosphere) to give 3.6 g (39%) of product, mp 66–69°. NMR (CDCl$_3$): δ 8.30–8.50 (m, 2, pyridyl H$_\alpha$), 7.17–7.55 (m, 10, C$_6$H$_5$), 6.88–7.17 (m, 2, pyridyl H$_\beta$). Anal. Calcd for C$_{17}$H$_{14}$PN: C, 77.56; H, 5.36. Found: C, 77.44; H, 5.54.

Oxidation of diphenyl-4-pyridylphosphine with a 10% aqueous solution of H$_2$O$_2$ in acetone gave 61% of the monoxide, mp 153–155°. NMR (CDCl$_3$): δ 8.56–8.90 (m, 2, pyridyl H$_\alpha$), 7.21–8.04 (m, 12, C$_6$H$_5$, pyridyl H$_\beta$). The ir spectrum (Nujol) showed the presence of a strong band due to the P–O stretching frequency[16] at 1195 cm^{-1} and the absence of any N–O stretching frequency.[17] Anal. Calcd for C$_{17}$H$_{14}$PNO: C, 73.11; H, 5.05; N, 5.02. Found: C, 73.16; H, 5.28; N, 4.96.

Table III. Spectral Parameters (cm^{-1}) for Cobalt(II) Complexes

	Co(P$^+$py)Br$_3$	Co(P$^+$pic)Br$_3$	Et$_4$N$^+$[Co-(C$_5$H$_5$N)Br$_3$]$^-$
ν_2[a]	6590	6500	6400
ν_3[b]	15,000	14,900	14,880
Dq[c]	380	375	370
B[d]	672	676	680
Δ[e]	2800	2680	2530

[a] Defined for T_d symmetry. Obtained by summing two-thirds of the ^{4}E component and one-third of the ^{4}A$_2$ component. [b] Obtained from the center of the band envelope, excluding the high-energy shoulder. [c] Dq obtained using the T_d equations for d^7 complexes and values of ν_2 and ν_3. Dq appears obtainable to within ±5 cm^{-1}. [d] Racah interelectronic parameter. B appears obtainable to within ±2 cm^{-1}. [e] Energy difference between the two components of ν_2.

Oxidation of diphenyl-4-pyridylphosphine with m-chloroperbenzoic acid gave 55% of the dioxide, mp 205–207.5°. NMR (CDCl$_3$): δ 8.10–8.41 (m, 2, pyridyl H$_\alpha$), 7.28–7.93 (m, 12, C$_6$H$_5$, pyridyl H$_\beta$). The ir spectrum showed both the N–O and P–O stretching frequencies. Anal. Calcd for C$_{17}$H$_{14}$PNO$_2$: C, 69.15; H, 4.78; N, 4.74. Found: C, 69.08; H, 4.81; N, 4.73.

Methyldiphenyl-4-pyridylphosphonium Bromide, (P$^+$py)Br. To a solution of 0.53 g of diphenyl-4-pyridylphosphine (2.0 mmol) in ether was added 0.50 g of an aqueous solution of HBr (2.9 mmol). The resulting precipitate was dissolved in ca. 60 ml of methyl bromide, and after stirring of the solution for 3 days in a pressure bottle, the adduct precipitated. The methyl bromide was allowed to evaporate, and the residue was dissolved in water and treated with ammonia. The product was then extracted into chloroform and was obtained by removing the solvent under vacuum, crystallizing the crude material from ethanol–ether, and recrystallizing from acetone; yield 0.46 g (64%); mp 269–270°. NMR (CDCl$_3$): δ 8.83–9.16 (m, 2, pyridyl H$_\alpha$), 7.60–8.26 (m, 12, C$_6$H$_5$, pyridyl H$_\beta$), 3.47 (d, J_{HP} = 14 Hz, 3, CH$_3$). Anal. Calcd for C$_{18}$H$_{17}$PNBr: C, 60.35; H, 4.78; Br, 22.31. Found: C, 60.17; H, 4.94; Br, 22.20.

Methyldiphenyl-4-picolylphosphonium Bromide, (P$^+$pic)Br. Methyldiphenylphosphine (1.5 g, 7.2 mmol) was added to 1.1 g of 4-(bromomethyl)pyridine (6.5 mmol) dissolved in 40 ml of ether. When the ether was removed under vacuum, an orange-white material formed, accompanied by a noticeable heat of reaction. After the reaction mixture had cooled, acetone was added to wash out unreacted phosphine. The undissolved residue was crystallized from methanol–ether, put on a column of 30 g of alumina (basic, activity I), and eluted with 200 ml of a chloroform–methanol (95:5) mixture. The solvent was removed under vacuum and the residue was crystallized from ethanol–ether to give 0.50 g (20%) of product, mp 224–225°. NMR (D$_2$O):[18] δ 8.30–8.60 (m, 2, pyridyl H$_\alpha$), 7.50–7.90 (m, 10, C$_6$H$_5$), 6.80–7.20 (m, 2, pyridyl H$_\beta$), 4.25–4.60 (m, 2, CH$_2$), 2.50 (d, J_{HP} = 13 Hz, 3, CH$_3$). Anal. Calcd for C$_{19}$H$_{19}$PNBr: C, 61.31; H, 5.14; Br, 21.41. Found: C, 61.06; H, 5.11; Br, 21.47.

Preparation of the Complexes.[12] Ethanol solutions of the anhydrous metal bromide were added to ethanol solutions containing an approximately equimolar amount of the cationic ligand. The solution was refluxed for a few minutes and the complex precipitated. It was filtered, washed with hot ethanol, and dried in vacuo over P$_2$O$_5$.

Supplementary Material Available. Table IV, containing analytical data for the complexes, and Figure 1, containing the electronic spectra in the region 24,000–40,000 cm^{-1}, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for

$4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40394H.

References and Notes

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(18) Chemical shifts in D2O are reported downfield from sodium 2,2-dimethyl-2-silacyclopentane-5-sulfonate as internal standard.

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Kinetics of Complexation of Copper(I) Ions with Maleate and Fumarate in Aqueous Solutions. A Pulse Radiolytic Study
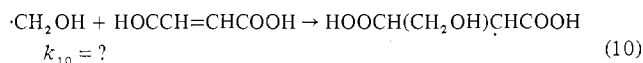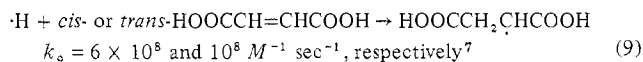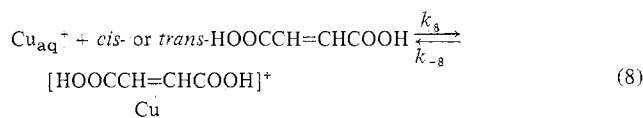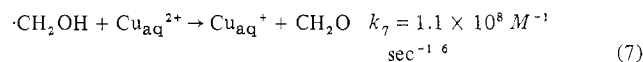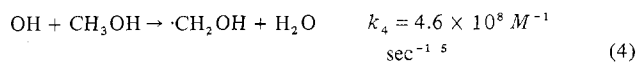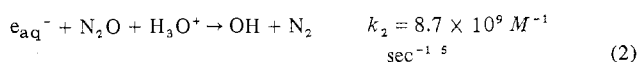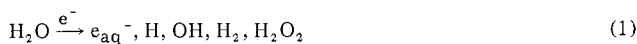
D. Meyerstein

Copper(I) ions form relatively stable complexes with organic compounds containing unsaturated carbon–carbon bonds.[1,2] These complexes have typical absorption bands in the near-uv region.[1,2] It seemed of interest to measure the kinetics of formation of such complexes. Thus, information concerning the rate of ligand exchange of copper(I) ions could be obtained. No data concerning the specific rate of ligand exchange of copper(I) have been reported to the best of our knowledge, though very high rates would seem reasonable for a monovalent d^{10} cation.

Results and Discussion

The pulse radiolytic technique was chosen for this study.[3] (The experimental procedure has been described elsewhere in detail.[4]) Nitrous oxide saturated solutions containing 1.0×10^{-2} M CuSO4, 1.0 M methanol, and 1.0×10^{-5}–1.0×10^{-3} M of fumaric or maleic acid at pH 3.65 ± 0.05 were irradiated by 2.5×10^{19} eV/l. pulse. Reactions 1–10 might occur under

$$H_2O \xrightarrow{e^-} e_{aq}^-, H, OH, H_2, H_2O_2 \tag{1}$$

$$e_{aq}^- + N_2O + H_3O^+ \rightarrow OH + N_2 \qquad k_2 = 8.7 \times 10^9 \ M^{-1} \ sec^{-1} \ [5] \tag{2}$$

$$e_{aq}^- + Cu_{aq}^{2+} \rightarrow Cu_{aq}^+ \qquad k_3 = 3.3 \times 10^{10} \ M^{-1} \ sec^{-1} \ [5] \tag{3}$$

$$OH + CH_3OH \rightarrow \cdot CH_2OH + H_2O \qquad k_4 = 4.6 \times 10^8 \ M^{-1} \ sec^{-1} \ [5] \tag{4}$$

$$H + CH_3OH \rightarrow \cdot CH_2OH + H_2 \qquad k_5 = 1.6 \times 10^6 \ M^{-1} \ sec^{-1} \ [5] \tag{5}$$

$$H + Cu_{aq}^{2+} \rightarrow Cu_{aq}^+ + H_3O^+ \qquad k_6 = 5 \times 10^8 \ M^{-1} \ sec^{-1} \ [5] \tag{6}$$

$$\cdot CH_2OH + Cu_{aq}^{2+} \rightarrow Cu_{aq}^+ + CH_2O \qquad k_7 = 1.1 \times 10^8 \ M^{-1} \ sec^{-1} \ [6] \tag{7}$$

$$Cu_{aq}^+ + cis\text{- or } trans\text{-HOOCCH=CHCOOH} \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} \begin{matrix} [HOOCCH=CHCOOH]^+ \\ Cu \end{matrix} \tag{8}$$

$$\cdot H + cis\text{- or } trans\text{-HOOCCH=CHCOOH} \rightarrow HOOCCH_2CHCOOH$$
$$k_9 = 6 \times 10^8 \text{ and } 10^8 \ M^{-1} \ sec^{-1}, \text{respectively}[7] \tag{9}$$

$$\cdot CH_2OH + HOCCH=CHCOOH \rightarrow HOOCH(CH_2OH)CHCOOH$$
$$k_{10} = ? \tag{10}$$

these conditions. (The yields of the radicals for eq 1 are[3] $G_{C_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.6$, $G_{H_2O_2} = 0.75$, and $G_{H_2} = 0.45$ where G is defined as the number of molecules of product formed by absorption of 100 eV by the sample). Reaction 9 competes with reactions 6 and 5 for the hydrogen atoms, but even at the highest concentration of the unsaturated acid used, 1×10^{-3} M, less than 15% of the H atoms react via reaction 9. As the hydrogen atom yield is about 10% of the total radical yield, the maximal effect of reaction 9 is to decrease the Cu(I) concentration by 2%. Reaction 10 was found by blank experiments carried out in the absence of Cu^{2+} to be slow relative to reaction 7 and can be neglected.

Therefore all the radicals formed under the experimental conditions reduce Cu_{aq}^{2+} to Cu_{aq}^+, and $G(Cu_{aq}^+) = 5.85$. (A somewhat higher yield is plausible due to the high solute concentrations.[8]) The formation of Cu_{aq}^+ ends within less than 2 μsec.

The absorption spectra of the products formed by the pulse were measured 50 μsec after the pulse and were stable for several minutes. The spectra are shown in Figure 1 with λ_{max}(copper(I) maleate) 345 ± 10 nm, ϵ_{max} 2800 $\pm$ 500 M^{-1} cm^{-1}, and λ_{max}(copper(I) fumarate) 335 ± 10 nm, ϵ_{max} 3000 $\pm$ 500 M^{-1} cm^{-1}. (In Figure 1 the observed optical densities, OD, and the molar absorption coefficients, ϵ, calculated from OD, the pulse intensity, and the total radical yield are shown. The figures given above are higher by 10% due to the fact that in solutions containing 1×10^{-3} M unsaturated carboxylic acid 10% of the Cu(I) is uncomplexed; see below.) No stable products having absorption in the 300–500 nm range were observed when either Cu_{aq}^{2+} or the unsaturated carboxylic acid were omitted from the solution or when malonic acid was used instead of the unsaturated carboxylic acid. The observed spectra are similar to those reported in the literature for the same complexes at pH O.[2] The small shifts in λ_{max} and the larger ϵ_{max} observed in this study are attributed to the partial acid dissociation of the carboxylic groups at pH 3.65.

The kinetics of formation of the absorption due to the Cu(I) complex always obeyed a pseudo-first-order rate law. The observed specific rates of reaction, k, are plotted against the unsaturated carboxylic acid concentration, C, in Figure 2. From the intercept and the slope of the straight lines obtained k_8 and k_{-8} can be calculated. ($k = k_8C + k_{-8}$ is predicted from the suggested mechanism.[9]) Thus for maleic acid $k_8 = (2.0 \pm 0.4) \times 10^9$ M^{-1} sec^{-1}, $k_{-8} = (1.8 \pm 0.4) \times 10^5$ sec^{-1}, and $K_8 = k_8/k_{-8} = (1.1 \pm 0.3) \times 10^4$ M^{-1} and for fumaric acid $k_8 = (1.7 \pm 0.4) \times 10^9$ M^{-1} sec^{-1}, $k_{-8} = (2.4 \pm 0.4) \times 10^5$ sec^{-1}, and $K_8 = (7.1 \pm 2.0) \times 10^3$ M^{-1} are obtained. The high specific rates of reaction 8 are in agreement with the expected rates of water exchange of Cu_{aq}^+ ions.

The stability constants of the complexes were also calculated from the effect of the unsaturated carboxylic acid concentration on the yield of the complex as measured by the optical density