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Binuclear Ions of Copper(I) and Certain Transition Metal Complexes and Kinetics of Electron Transfer between Metal Centers

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Abstract: Cuprous ion binds strongly to organic acids containing unsaturated carbon–carbon bonds and their pentaamminecobalt(III) and pentaaquochromium(III) complexes, forming adducts of 1 : 1 stoichiometry. Formation constants for the $(NH_3)_5Co^{III}$–acrylato–$Cu^{I\,3+}$ and $(NH_3)_5Co^{III}$–fumarato–$Cu^{I\,3+}$ ions are $K = 4 \pm 3 \times 10^4$ M^{-1} and $4.4 \pm 2 \times 10^3$ M^{-1}, respectively, in 1.0 M $HClO_4$ at 23°. For the latter ion, $\Delta H° = -11.5 \pm 3.2$ kcal/mol and $\Delta S° = -22 \pm 10$ eu at 23°. Bonding is adequately accounted for by a simple π-complexation scheme. The complexes are characterized by copper metal-to-ligand charge-transfer transitions appearing in the near-uv region. The pentaamminecobalt(III)–cuprous ion dimers undergo net electron transfer only very slowly, but electron transfer between metal centers can be photoinduced by irradiation of either cobalt d–d or copper → ligand charge-transfer bands. Implications of the results concerning electron-transfer mechanisms are discussed.

Electron transfer between transition metal ions apparently occurs in several discrete steps, *i.e.*, association of reactant ions, electron transfer, and dissociation of product ions.[1–6] Each of the processes might be complex. For the class of reactions designated as inner sphere, ion association includes ligand substitution at one of the reactant metal centers to produce ligand-bridged dimers, denoted precursor complexes. Following electron transfer product dimers decompose in further ligand substitution steps. Any of these steps might be rate determining, but useful information concerning the electron-transfer process can be had from kinetic studies only if one of the latter steps is slowest. For these cases, precursor complexes are almost invariably undetectable in reaction solutions and measured rate parameters are functions of several variables; *e.g.*, for rate-limiting electron transfer, $k_{obsd} = Kk_{et}$, where K is the precursor complex formation constant and k_{et} the intrinsic electron-transfer rate constant. Analysis of reaction mechanisms by systematic alteration of reactant structure is thereby confounded since effects upon rate parameters due to varying precursor complex stabilities and intrinsic electron-transfer processes cannot be separated.[1,7]

Cuprous ion coordinates strongly to unsaturated carbon–carbon bonds[8,9] and transfers an electron only very slowly to Ro–carboxylato[10] complex ions.[11] This combination of properties makes solutions of Cu(I) with Ro–olefin acids optimally suited for direct observation and quantitative characterization of precursor complexes. In studying the binding process, we have taken advantage of the large changes in electronic absorption spectra that accompany Cu(I) complexation in these solutions.[12,13] Preliminary rate data for electron transfer in the reactant dimers are also given in this report.

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(10) Abbreviations used in this text: Ro–, $(NH_3)_5Co^{III}$ moiety; Cr(III)–, $(H_2O)_5Cr^{III}$ moiety; acr, acrylate; fum, fumarate; mal, maleate; cin, cinnamate; pro, propiolate; vin, vinylacetate; all, allylacetate.

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Experimental Section

Reagents. Carboxylatopentaamminecobalt(III) perchlorate complexes were generally prepared by equilibrating aqueous or dimethylformamide (DMF) solutions of the Ro–aquo complex at 60–70°, pH 4–5, for several hours with a large excess of the organic acid. Ro–terephthalato perchlorate was prepared according to Nordmeyer,[14] and Ro–pyridine and Ro–isonicotinamide complexes were prepared by the method of Nordmeyer and Taube.[15] All complexes were recrystallized several times from hot dilute perchloric acid and dried by washing successively with ethanol and diethyl ether. The product complexes were characterized by quantitative determinations of their electronic absorption spectra in acid and alkaline solutions and by proton nmr analysis. Molar extinction coefficients measured for the recrystallized RoL complexes were in good agreement with published values. Spectra showed only very slight pH dependencies, spectral shifts, and changes in band intensity, when observed, being consistent with the presence of a few per cent Ro–aquo impurity. For all complexes the nmr spectra agreed with that anticipated from considering spectra of the corresponding uncomplexed organic acids. No Ro–DMF impurity was observed in spectra of recrystallized RoL complexes prepared in DMF solvent, although spectra taken of the complexes at intermediate stages of the preparations clearly indicated the presence of Ro–DMF ion. Two relatively broad transitions ascribable to protons on NH_3 groups coordinated cis and trans to the organic ligand were also observed, except for Ro–pyridine perchlorate. Sharp proton lines appeared in the aromatic region for this ion so we are unable to offer an explanation for its anomalous behavior with respect to the ammine protons.

Carboxylatopentaaquochromium(III) ions were generated *in situ* by reduction of Ro–carboxylato ions with an equimolar quantity of Cr(II) and were not isolated from the other reaction products. Chromous ion was prepared by reduction of deoxygenated standard chromic perchlorate solutions over amalgamated zinc. Chromium(III) solutions were prepared by reduction of acidic potassium dichromate solutions with hydrogen peroxide and analyzed by spectrophotometric determination of the concentration of aliquots oxidized in alkaline solution with hydroperoxide to chromate ion.[16]

Cuprous ion was routinely prepared by partial reduction of deoxygenated cupric perchlorate solutions with chromous ion according to the procedures described by Shaw and Espenson.[17] Cupric ion was generally in *ca.* tenfold excess. Concentration levels of Cu(I) were generally sufficiently high that the aqueous solutions were metastable, Cu(I) disproportionating within several hours unless stabilized by addition of suitable coordinating agents. Solutions were therefore used immediately after preparation, sufficient time being given after mixing reagents for the reactions to proceed >98% to completion. In a few instances Cu(I) was also generated by equilibration of deoxygenated concentrated Cu(II) solutions with added copper metal.

Cupric perchlorate hexahydrate used for infrared studies was recrystallized several times from deuterium oxide (Bio-Rad, 99.88 mol %) to replace "waters of crystallization" with D_2O. Chromic solutions were likewise prepared by dissolving crystalline chromic perchlorate in D_2O. Spectrochemical grade acetonitrile (Matheson Coleman and Bell) and polarographic grade tetrabutylammonium perchlorate (Southwestern Analytical Chemicals) were used to prepare solutions for polarographic measurements. Other chemicals were reagent grade and used without further purification.

Difference Spectral Measurements. Electronic absorption spectra of deoxygenated solutions containing cuprous ion and carboxylic acids or RoL or chromium(III) carboxylato ions, referenced against air, were recorded. Solutions were then thoroughly oxygenated and the spectra rescanned. Observed difference spectra were corrected for the spectral change due to oxidation of Cu(I) by subtracting the independently determined spectral difference between solutions containing only cuprous and cupric ions. The corrected difference curves thus obtained measure just spectral changes accompanying the mixing of Cu(I) with the other ions.[18]

Air-sensitive reagents were usually prepared in vessels stoppered with serum caps and transferred and mixed with hypodermic syringes, although occasionally reagents were prepared and manipulated in an all-glass apparatus. No discrepancies in the results obtained with the two methods were noticed. Electronic absorption spectra were recorded on Cary Model 15 or 16 spectrophotometers, the latter outfitted with a slit servo mechanism and recorder interface. Cell blocks were thermostated by recirculating water from constant-temperature baths. Actual cell temperatures were determined by measuring voltages of an attached copper–constantan thermocouple referenced against an ice–water bath. Solutions containing Cu(I) and certain RoL ions are photosensitive (*vide infra*) and were protected from the light when spectra were not being recorded.

Infrared Spectral Measurements. Infrared absorption spectra of concentrated D_2O solutions of acrylic and fumaric acids and their Ro and Cr(III) complexes with cuprous ion were determined in the "window" region 2000–1300 cm^{-1} using a Perkin-Elmer 621 recording spectrophotometer. Spectra both of Cu(I) containing solutions and the corresponding oxygenated solutions, referenced against a variable beam attenuator, were recorded. Barnes Engineering demountable cells, 0.05-mm path length, equipped with Irtran II (ZnS) windows and modified by replacing metal Luer hubs with Kel-F hubs and coating exposed metal with epoxy resin, were used in the measurements. Preliminary experiments had indicated that the reagent solutions reacted with the metal components of the ir cell and these modifications effectively diminished that reaction.

Raman spectra of concentrated cuprous solutions of fumaric and acrylic acids and their Cr(III) complexes, and of the corresponding oxygenated solutions, were recorded using a Jarrel-Ash 25-300 Raman spectrometer. The excitation source was the 4880-Å line from an Ar^+ ion laser, operated at *ca.* 0.5 W and directed into a single pass cell containing the reactant ions.

For both measurements dilute reagent solutions were initially prepared, then mixed and concentrated by vacuum distillation of solvent. The final solutions were transferred to an oxygen-free environment (Vacuum Atmospheres Corp. Drilab) where optical cells were loaded.

Polarographic Measurements. Electrochemical waves for reduction at the dme of a series of organic methyl esters in acetonitrile (0.1 *M* tetrabutylammonium perchlorate) were measured using a three-electrode system based upon the operational amplifier circuits of Booman.[19] Platinum foil and Ag wire immersed in 0.01 *M* $AgNO_3$, 0.1 *M* $(C_4H_9)_4NClO_4$, CH_3CN solution served as counter and reference electrodes, respectively. The reference electrode was separated from the electrolysis solution by a Vycor plug. Polarograms were recorded on an EAI Model 1131 Variplotter X-Y recorder without damping. Reagents and electrolysis cell were located in the Drilab glove box to minimize uptake of H_2O during solution preparations and measurements. Polarographic background currents were always less than 0.15 μA topotentials as negative as -3.1 V, at which point reduction of solvent commenced.

Kinetic Measurements. Rates of electron transfer between cuprous ion and RoL complexes containing alkenoic acids as the unique ligands (L) were monitored by determining the amount of Co(II) formed as a function of time. Cobaltous ion was analyzed as $CoCl_4^{2-}$.[20] The reaction solution also contained relatively high concentrations of Cu(II) which gave rise to strong background absorption in the $CoCl_4^{2-}$ spectral region. Samples comprising oxygenated aliquots of the reaction solution were therefore prepared as reference solutions. Reaction solutions were protected from light to preclude photochemical reactions.

Rates of photochemically induced electron transfer between cuprous ion and Ro–carboxylato complexes and rates of photodecomposition of the RoL complexes were studied. Experimental results described were obtained using as illumination source a Hanovia 200-W high-pressure mercury–xenon compact arc lamp mounted in a Bausch & Lomb mercury light source housing and powered by a Kepco KS 60-20M supply. Emitted light was passed into a Bausch & Lomb high-intensity visible–ultraviolet grating monochromator equipped with an achromatic condenser lens, then through the reaction cell. The radiant flux from the monochromator was not determined, but for all wavelengths slit widths were adjusted to give a spectral bandpass of 25 nm. Solutions were irradiated at

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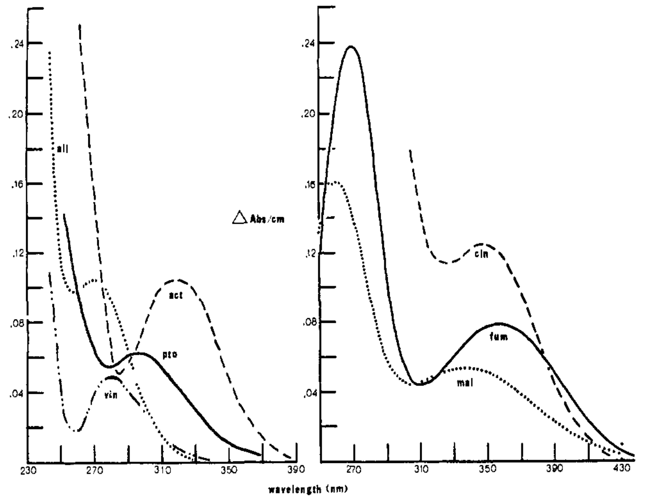

Figure 1. Cu(I)-unsaturated carboxylic acid difference spectra. $(RCOOH)_T = (Cu(I))_T = 2.5 \times 10^{-4}$ *M;* 1.0 *M* $HClO_4$; 23°. Abbreviations are defined in ref 10.

503 nm for as long as 25 hr or at wavelengths corresponding to the lowest energy near-uv difference spectral maxima (*vide infra*) for 1-2 hr. A plate glass filter was placed in the light path between the monochromator and reaction cells in the excitation studies with visible light to exclude higher order wavelengths and high energy stray light. The photochemical reactions were interrupted periodically to record electronic absorption spectra. Analyses for Co(II) produced were made at the end of each irradiation run using the $CoCl_4^{2-}$ method. Estimates of RoL and Cu(I) consumed were made from spectral changes observed at 503 nm and the difference wavelength maxima, respectively.

Results

Electronic Spectra. Two new absorption bands appear in the near-ultraviolet spectrum when solutions containing cuprous ion and alkenoic acids (or propiolic acid) are mixed. In Figure 1, the corrected difference absorptions, which measure the deviations from Beer's law observed for these solutions, are plotted as a function of wavelength. Analogous spectra were obtained for solutions containing Cu(I) and the corresponding organic acids coordinated to Ro or Cr(III) groups. In these complex ions, absorption maxima for at least the first transition are generally displaced slightly toward higher energies relative to the free carboxylic acids (Table I).[21]

Table I. Frequency Maxima for Cu^I-Organic Acid Interactions[a]

	Acid (L) λ_{max}, nm	RoL^{2+} λ_{max}, nm	$Cr^{III}L^{2+}$ λ_{max}, nm
fum	358, 270	348, 270	352, 269
mal	340, 260	343, 265	
acr	318	305	315, 250
cin	345	340	
pro	303	285	
vin	280	280	
all	276	280	

[a] In 1.0 *M* $HClO_4$, 23°; abbreviations defined in ref 10.

No difference absorptions were detected in solutions containing Cu(I) and Ro-carboxylato complexes whose organic ligands contain any of a variety of functional groups but do not possess simple carbon-carbon unsaturated bonds. Compounds tested include those with acetate, proprionate, glycolate, lactate, pyruvate, oxalate, succinate, benzoate, terephthalate, pyridine, isonicotinamide, and aquo ligands.

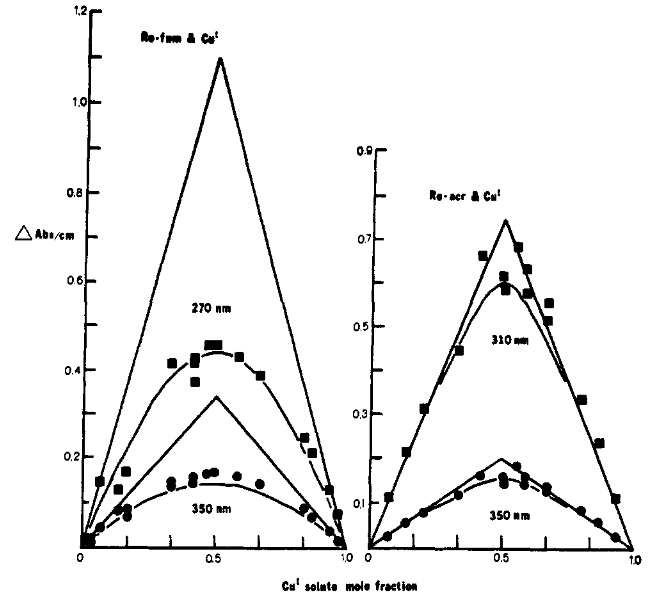

Figure 2. Job diagrams $(RoL + Cu(I))_T = 5 \times 10^{-4}$ *M;* 1.0 *M* $HClO_4$; 23°.

No deviations from Beer's law were seen in 1.0 *M* $HClO_4$ solutions of $AgClO_4$ with the Ro-carboxylato complexes which exhibit interaction absorptions with Cu(I) under the conditions (Ag(I)) = 0.1 *M*, (RoL) = 10^{-2} *M*, λ 800-300 nm; (Ag(I)) = 10^{-3} *M*, (RoL) = 10^{-4} *M*, λ 300-200 nm.

Quantitative investigations of the cuprous interactions with the Ro-fumarato and Ro-acrylato ions were made. The method of continuous variations[22] was applied to ascertain the stoichiometry of the cobalt-copper complexes producing the difference absorptions. Results are given in Figure 2. For the Ro-fumarato complex, the data presented correspond to the frequency maxima of the first and second difference absorption bands. The symmetrical appearance of these Job plots argues for the predominant formation of 1:1 complexes. No evidence for adducts of different stoichiometry was found when spectra corresponding to much wider variation in reagent concentrations were compared. Relative intensities of the difference absorptions as a function of wavelength were constant for solutions containing from 30-fold excess Cu(I) to 40-fold excess RoL, specifically over the ranges (Ro-fumarato) = (0.16-200) × 10^{-4} *M*, Cu(I) = (2.5-5.0) × 10^{-4} *M*, λ 400-270 nm; (Ro-acrylato) = (2.5-100) × 10^{-4} *M*, Cu(I) = (2.5-5.0) × 10^{-4} *M*, λ 400-280 nm.

Equilibrium constants for formation of the mixed dimers were calculated from difference spectra of solutions with widely varying reagent concentrations using a method of successive approximations described by Hammes and Schimmel.[23] Best fit values of *K* and

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(21) It proved extremely difficult to obtain data at wavelengths shorter than *ca.* 300 nm. Strong background absorptions arising principally from internal transitions of the organic ligands and, for the Ro complexes, ligand-to-metal charge transfer transitions commence in this region and prevent accurate measurement of the difference absorptions.

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Table II. Equilibrium Constants for Dimer Formation[a]

Equilibrium	T, deg	$10^{-3}K$, M^{-1} [b]	λ_{max}, nm	$10^{-3}\Delta\epsilon_{max}$[b]
Ro-fum + Cu(I) $\rightleftharpoons$ Ro-fum-Cu(I)	5	15 ± 3	349	
	23	4.4 ± 2.0	350, 270	1.4 ± 0.3, 4.4
	40	1.5 ± 0.6	351	
Ro-acr + Cu(I) $\rightleftharpoons$ Ro-acr-Cu(I)	23	40 ± 30	310	1.5 ± 0.3

[a] In 1.0 M $HClO_4$; abbreviations defined in ref 10. [b] Error limits are the range of values obtained for minimization of several sets of data.

$\Delta\epsilon$ ($= \epsilon_{RoLCu} - \epsilon_{RoL} - \epsilon_{Cu}$) are given in Table II. These values were used to calculate theoretical binding curves which are shown as the solid lines on the Job plot diagrams (Figure 2). The best fit results represent averages of 23 runs in the Ro-fum-Cu(I) system, reagent concentrations being varied over the ranges $(RoL)_T = (1.67\text{–}400) \times 10^{-4}$ M, $(Cu(I))_T = (0.83\text{–}5.0) \times 10^{-4}$ M, and averages of 34 runs in the Ro-acr-Cu(I) system, reagent concentrations being varied over the ranges $(RoL)_T = (0.67\text{–}100) \times 10^{-4}$ M; $(Cu(I))_T = (0.71\text{–}9.4) \times 10^{-4}$ M. Approximate oscillator strengths (f) calculated for the dimer absorption bands using the relation, $f \approx 4.6 \times 10^{-9}\epsilon_{max}\Delta\nu$, where $\Delta\nu$ is the half-band width in cm^{-1}, are, for Ro-fum-Cu(I), $f_{350} \approx 0.04$, $f_{270} \approx 0.10$; for Ro-acr-Cu(I), $f_{310} \approx 0.05$ at 23°.

Dimer spectra exhibited only slight temperature dependence. For Ro-fum-Cu(I) ion in 1.0 M $HClO_4$, Δabsorbance relative intensities at various wavelengths over the range 450–300 nm were nearly constant, the absorption bands broadening slightly as the temperature was increased from 5 to 40°. Maximal difference absorptions for 1.0 M $HClO_4$ solutions containing concentration levels of the fumaric acid (0.03 M), acrylic acid (0.01 M), or Ro-acrylate (1.0×10^{-3} M) sufficiently high to coordinate essentially completely[24] (>95% at 23°) added cuprous ion, $(Cu(I))_T = 5 \times 10^{-4}$ M, decreased only a few per cent with increasing temperature. At the highest Ro-fumarate concentrations attainable, absorbance values decreased *ca.* 25% with increasing temperature, but the magnitude of this change was consistent with decreased association of the ions with increasing temperature (*vide infra*). Frequency maxima for all these dimers underwent small bathochromic shifts with increasing temperature, shifting *ca.* 1–2 nm for every 20° rise in temperature. Temperature effects observed for these difference spectra were fully reversible. Data for Ro-fum-Cu(I) are reported in Table II.

Equilibrium constants for formation of the Ro-fum-Cu(I) dimer were determined at various temperatures from the measured Δabsorbance values, assuming $\Delta\epsilon$ to be temperature independent. Several determinations were made in 1.0 M $HClO_4$, varying Ro-fumarato and Cu(I) ions over the ranges, $(Ro\text{-}fum)_T = (2.5\text{–}10.0) \times 10^{-4}$ M, $(Cu(I))_T = (2.5\text{–}5.0) \times 10^{-4}$ M. Results are given in Table II. Thermodynamic parameters, evaluated from the relationships $d(\log K)/d(1/T) = -\Delta H°/2.3R$, $\Delta G° = \Delta H° - T\Delta S°$ are: $\Delta H° = -11.5 \pm 3.2$ kcal/mol, $\Delta S° = -22 \pm 10$ eu at 23°. The limits cited were determined from maximum and minimum slopes for the van't Hoff plot drawn to be consistent with error limits for the individual points.

Competitive binding studies involving the Ro-benzoato, Ro-terephthalato, and Ro-isonicotinamido ions in competition with the Ro-acrylato ion for Cu(I) were undertaken to determine whether cuprous ion might bind these ligands. No evidence of diminution of the Ro-acr-Cu(I) difference spectrum was seen, even in the presence of up to 80-fold excess of the other complex ion. All measurements were made at 23° in 0.1–1.0 M $HClO_4$. Based upon these results, upper limits for the equilibrium constant for Cu(I) binding to these ions were placed at $K \leq 10^2$ M^{-1}.

Vibrational Spectra. Raman spectra of concentrated solutions of acrylic acid, chromium(III) acrylate and chromium(III) fumarate gave strong vibrational bands at 1640–1660 and 1275–1285 cm^{-1} which shifted to 1520–1525 and 1236–1240 cm^{-1} upon coordination to Cu(I). The bands in the 1650- and 1520-cm^{-1} regions are assigned to C=C stretching modes for the organic ligands and their Cu(I) complexes, respectively. Additional transitions ascribable to the acids are weak and shift imperceptibly with Cu(I) coordination. Concentration levels of Cr(III)-fum-Cu(I) ion did not change after exposure to excitation by the Ar$^+$ laser for periods up to *ca.* 1.5 hr, indicating that no photoredox processes had occurred during recording of the spectra. Similarly, the absence of detectable shifts in wavelength maximum of Δabsorbance for Cr(III)-acr-Cu(I) after recording the Raman spectrum indicated negligible photoaquation of that ion.

Absorption bands at 1690 cm^{-1} were clearly evident in the infrared spectrum of concentrated solutions of Cu(I) complexes with fumaric and acrylic acids. Similar bands appeared at 1640 cm^{-1} in the Ro- and Cr(III)-acr-Cu(I) dimer spectra, while the Ro- and Cr(III)-fum-Cu(I) spectra exhibited both carbonyl stretching modes for protonated (1690 cm^{-1}) and metal-coordinated (1640 cm^{-1}) carboxyl groups. With the single exception of the acrylate dimers, oxygenation of these solutions was accompanied by an increase in the intensity of the transitions due to metal ion coordinated carboxyl groups relative to those for the COOH group. The 1640/1690 cm^{-1} ratio was also found to increase in a reference spectrum of acrylic acid with addition of increasing concentrations of cupric ion. Analyses for dimer concentrations made before and after scanning the ir spectrum agreed favorably indicating negligible decomposition of the complexes occurred during the course of obtaining the data.

Polarographic Reduction Behavior. Single reduction waves were observed at the dme for CH_3CN–0.1 M $(C_4H_9)_4NClO_4$ solutions of the methyl esters of the conjugated unsaturated carboxylic acids investigated here. No cathodic waves were observed for vinylacetate and allylacetate methyl esters to potentials as negative as -3.05 V. Results are given in Table III. The n values recorded, which represent the number of

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[24] Formation constants for Cu(I) binding to alkenoic acids in 0.1 M $HClO_4$, 25°, have been determined by measuring changes in solubility of CuCl in the presence of the organic acids. Values of $K \simeq 10^4$ are reported for these interactions.[8]

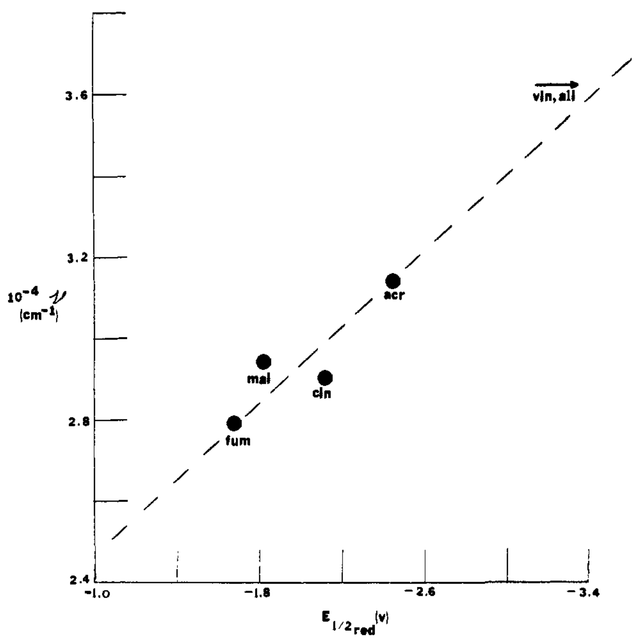

Figure 3. Correlation of transition frequencies for Cu(I)-alkenoates with half-wave reduction potentials for the ligand esters. The arrow indicates that $E_{1/2}$ values for Me-vin and Me-all are more negative than −3.05 V. Abbreviations are defined in ref 10.

Table III. Polarographic Reduction Data[a]

Ester[b]	$E_{1/2}$ (red),[c] V	I	n	αn
Me$_2$-fum	−1.685	1.89	0.76	1.1
Me$_2$-mal	−1.82	1.89	0.75	0.67
Me-cin	−2.14	3.18	1.29	1.05
Me-acr	−2.46	1.95	0.73	0.48
Me-pro	−2.36	2.9	1.08	0.30
Me-vin	<-3.05			
Me-all	<-3.05			

[a] (Ester) = 2×10^{-3} M in CH$_3$CN, 0.1 M (C$_4$H$_9$)$_4$NClO$_4$, 23°. [b] Abbreviations defined in ref 10. [c] Relative to Ag|0.1 M Ag$^+$ (CH$_3$CN, 0.1 M (C$_4$H$_9$)$_4$NClO$_4$).

electrons transferred at the electrode surface, were calculated from the Ilkovic equation $I = 607nD^{1/2}$.[25] Slopes of the diffusion current curves, given as αn values, were determined from the equation

$$E_{1/4} - E_{3/4} = 0.0564/\alpha n$$

where $E_{1/4}$ and $E_{3/4}$ are the potentials for which the current is equal to one-fourth and three-fourths the diffusion current, respectively.[25]

Half-wave potentials for reduction of the methyl alkenoates are compared in Figure 3 with the frequency maxima for the first difference absorption bands of the corresponding Cu(I)-carboxylic acid complexes. A rough linear correlation is apparent.

Kinetic Studies. Solutions whose composition was $(\text{RoL})_T = 10^{-3}\ M$, $(\text{Cu(I)})_T = 5 \times 10^{-4}\ M$, $(\text{HClO}_4) = 1.0\ M$, were mixed and stored for several days at ambient temperature, then analyzed for cobaltous ion. Only for the reactions with Ro-cinnamate and Ro-propiolate could Co(II) be detected in the reaction solution. Spectral changes occurring during the reaction time period were consistent with some aquation of the RoL complexes. Reaction half-times for electron transfer for Ro-cin-Cu(I) and Ro-pro-Cu(I), assuming the reaction is first order, are $t_{1/2} > 50$ days. Based upon reasonable estimates of the sensitivity of the analytical method employed, half-times for the other Ro-L-Cu(I) ions are set at $t_{1/2} > 5$ years.

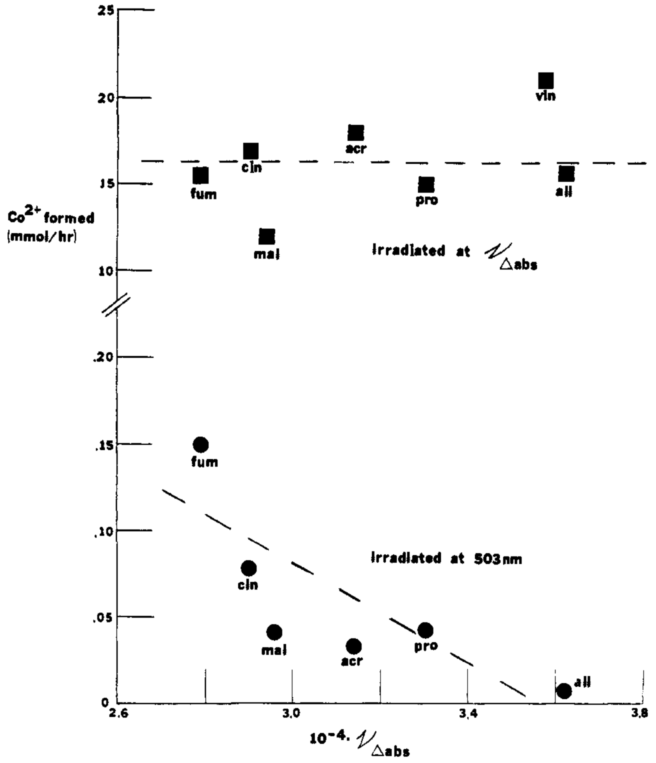

Figure 4. Photochemical induction of electron transfer in RoL-Cu(I) dimers. $(\text{RoL})_T \simeq 2 \times 10^{-3}\ M$; $(\text{Cu(I)})_T \simeq 10^{-3}\ M$; $(\text{HClO}_4) = 1.0\ M$; 23°. Reaction rates in solutions irradiated at $\nu_{\Delta abs}$ were determined from the absorbance decrease at 503 nm; those in solutions irradiated at 503 nm from the total Co^{2+} produced over the course of the runs. Abbreviations are defined in ref 10.

The cobalt-copper dimers rapidly decompose when irradiated with high-intensity visible or ultraviolet light. Solutions whose compositions were identical with those studied for thermal reactions were irradiated at 503 nm and at the frequency maxima for the first interaction absorption bands. Reference solutions comprising the corresponding oxygenated reactant solutions were also irradiated. No photodecomposition of the RoL complexes was detected after irradiation at 503 nm for 24 hr. Spontaneous decomposition did occur with irradiation with the higher energy light, but in no case did the rate exceed 5% of the total rate measured in the presence of Cu(I). Results are presented in Figure 4 where reaction rates are correlated with the difference frequency maxima. Reaction solutions containing Cu(I) and Ro-succinato or Ro-aquo ions, $(\text{RoL})_T = 2 \times 10^{-3}\ M$, $(\text{Cu(I)}) = 1 \times 10^{-3}\ M$, $(\text{HClO}_4) = 1.0\ M$, were irradiated at 350 nm for *ca.* 1.5 hr without any change occurring in reagent concentrations.

For solutions irradiated at the difference frequency maxima, analyses for Co(II) produced and RoL$_T$ and Ro-L-Cu(I) consumed generally agreed, suggesting 1:1 stoichiometry for net oxidation-reduction between metal centers. Exceptions were observed in the systems containing unconjugated organic bridging groups, *i.e.*, Ro-vin-Cu(I) and Ro-all-Cu(I), for which the concentration of RoL complex reduced exceeded that of Cu(I) present.

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(25) *Cf.* L. Meites, "Polarographic Techniques," 2nd ed Wiley, New York, N. Y., 1965.

Discussion

Cuprous ion interacts with unsaturated organic acids and their Ro or Cr(III) complexes to form adducts of 1:1 stoichiometry. Complexes of other stoichiometry are not evident, either from the Job plots of interactions of Cu(I) with Ro–fumarato and Ro–acrylato ions or from their difference spectra, the shapes of which do not vary with widely varying reagent concentration ratios. Coordination occurs almost certainly through the carbon–carbon double or triple bond in these complexes. Difference spectra appear only for those RoL complexes containing organic ligands possessing simple carbon–carbon unsaturation. RoL complexes with ligands containing aromatic rings and pendant carboxyl or amide groups did not compete effectively with Ro-acrylato ion for Cu(I) ion coordination. Further, coordination of Cu(I) to the acrylate and fumarate species was shown to cause bathochromic shifts of 120–135 cm^{-1} in the vibrational band assigned to the C=C stretching normal mode without significantly altering other features of the infrared spectra. This behavior is analogous to that observed for Cu(I) π complexation to unsaturated carbon–carbon bonds in other systems.[26]

In view of the presence of several potential coordinating groups on the organic ligands it is of interest to inquire whether one or several isomeric 1:1 π complexes are formed. Several lines of evidence suggesting that single unchelated species predominate in solution are summarized as follows.

(a) The slight temperature dependence of the spectra observed for cuprous ion π complexes of acrylic and fumaric acids and their RoL complexes can quite adequately be rationalized in terms of thermal broadening and shifts in binding equilibria without invoking the presence of more than one chromophore; particularly significant is the observation that the relative intensities of spectral maxima at 270 and 350 nm for Ro–fum–Cu(I) are temperature independent.

(b) No curvature was observed in the van't Hoff plot for the Ro–fum–Cu(I) system, consistent with the presence of a single dimeric species.

(c) Carbonyl stretching frequencies observed for pendant RCOOH ($\nu \simeq 1690\ \mathrm{cm}^{-1}$) and metal-coordinated RCOOM ($\nu \simeq 1640\ \mathrm{cm}^{-1}$) groups do not shift perceptibly with cuprous ion coordination. The increase in 1640/1690 cm^{-1} intensity ratio with oxygenation of dimer solutions strongly suggests that Cu^{2+}, present in high concentrations, is capable of binding to pendent carboxyl groups but only when Cu(I) is not π-coordinated. Given this interpretation, we infer that Cu(I) does not coordinate effectively to the COOH group.

(d) Other studies which compare formation constants for Cu(I) with unsaturated alcohols and carboxylic acids indicate stronger binding to alcohols than to the corresponding acids.[8,9] Should coordination involve chelation in the latter, we might expect to find that this interaction free energy would stabilize the Cu–ligand bond resulting in increased association to carboxylic acids rather than the observed behavior.

We conclude that Cu(I) coordination in these systems can best be described by the simple Dewar–Chatt–Duncanson π-complexation scheme,[27,28] which involves synergistic σ-bond formation between occupied π ligand and empty metal orbitals and π-bonding with back-donation from occupied metal orbitals to π^* orbitals on the ligand.

The new absorption bands appearing with formation of these cuprous π complexes originate most likely from charge-transfer transitions between copper and the ligands. These bands are of lower energy than those corresponding to either internal transitions on the ligand or ligand-to-metal charge-transfer transitions of the RoL and Cr(III) ions; their intensity, frequency dependence upon the identity of ligand, and approximate independence of the presence or identity of trivalent metal ion indicate that they are not internal d–d transitions of the metal ions; and oscillator strengths and ϵ values determined for Ro–fum–Cu and Ro–acr–Cu are of the proper magnitudes for charge-transfer transitions.[29]

Contact charge transfer[30] apparently contributes insignificantly to the difference absorption spectra. Spectra for the cuprous complexes of acrylate and fumarate species are relatively temperature independent, ϵ values increase (slightly) with binding free energies, and equilibrium constants for RoL–Cu dimer formation determined using optical methods are approximately the same magnitude as K values for Cu(I) association to the free olefin acids determined using nonoptical methods.[8]

Both metal-to-ligand and ligand-to-metal charge-transfer transitions are conceivable for Cu(I) π complexes. Correlation of charge-transfer transition energies with ligand orbital energies affords a means of distinguishing between these processes.[31,32] Estimates of relative electron affinities for the series of ligands were obtained from the half-wave potentials measured for the polarographic reduction waves of the corresponding methyl esters.[33] The polarographic results are in substantial agreement with the qualitative behavior expected for group substitution at the double bond;[32,37,38] *e.g.*, based upon Hammett σ values, π-donor and -acceptor orbital energies should increase along the series fumarate $\simeq$ maleate $<$ cinnamate $<$ acrylate $<$ vinylacetate $\simeq$ allylacetate. Through the

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(26) *Cf.* M. L. H. Green, "Organometallic Compounds," Vol. 2, G. E. Coates, M. L. H. Green and K. Wade, Ed., Methuen, London, 1968.

(27) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

(28) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939, (1953).

(29) *Cf.* T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 4, and references therein.

(30) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 71, 2703 (1949).

(31) G. Briegleb, *Angew. Chem., Int. Ed. Engl.*, 3, 617 (1964).

(32) R. Foster, "Organic Charge Transfer Complexes," Academic Press, New York, N. Y., 1969, Chapter 3, and references therein.

(33) Provided that the waves represent reversible one-electron processes, an approximate linear correlation between half-wave potential ($E_{1/2}$) and electron affinity (A) obtains;[31,32,34,35] *i.e.*, $E_{1/2} \simeq A +$ constant. The polarographic system employed was designed to minimize the concentration of proton donors which would decrease the likelihood of irreversible reduction of the esters, *e.g.*, as in ECE-type mechanisms.[36] The electrode reactions correspond closely to one-electron reductions, but only methyl fumarate and methyl cinnamate meet the criterion for reversibility that n values determined from the magnitude of diffusion currents and slopes coincide (Table III).

(34) A. Maccoll, *Nature* (*London*), **190**, 1003 (1961).

(35) M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970).

(36) J. Janata and H. B. Mark, *J. Phys. Chem.*, 72, 3616 (1968).

(37) A. Buchs, *Helv. Chim. Acta*, **53**, 2026 (1970).

(38) D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970).

ligand series the correlation of increasing transition frequency of the lowest energy difference absorption band with increasing energy of ligand acceptor orbital (Figure 3) is consistent with its assignment as a metal-to-ligand charge-transfer transition and inconsistent with the transition being ligand-to-metal. The small hypsochromic shifts in transition frequency of the first band generally observed with metal ion coordination to the carboxyl group also supports the M → L assignment, since metal ion replacement of a proton will increase electron density in the carbon–carbon unsaturated bond. In addition, the absence of detectable charge-transfer bands in the visible–near-ultraviolet regions for solutions of Ag(I) and RoL, measured under conditions for which appreciable π-complex formation undoubtedly occurs,[39] argues against L → M assignments for the transitions, Ag(I) being reduced considerably more readily than Cu(I).

The free energy change for net electron transfer from copper to cobalt in these systems is extremely favorable; *e.g.*, for the reaction

$$\mathrm{RoL^{2+} + Cu^{+} + 6H^{+} \longrightarrow Co^{2+} + Cu^{2+} + 5NH_4^{+} + HL}$$

the net driving force is 50–60 kcal/mol. The free-energy change for electron transfer in the dimers, *i.e.*, for the process

$$\mathrm{RoLCu^{I} \rightleftharpoons (NH_3)_5Co^{II}L + Cu^{II}}$$

was calculated from the oxidation potentials for the free ions[40] and measured precursor complex formation constants to be $\Delta G^\circ \simeq 0.8$, 2.1 kcal/mol for the ions Ro–fum–Cu(I) and Ro–acr–Cu(I), respectively. This value sets a lower limit upon the activation free energy required for the electron-transfer process. Despite the thermodynamic favorability, electron transfer is extremely slow and can be detected only in the complexes containing propiolic and cinnamic acid ligands.

In contrast to the kinetic behavior of the ground-state molecules, electron transfer between metal centers is markedly photoaccelerated, both when electronic transitions on cobalt and when copper–ligand charge-transfer transitions are induced.

The efficiency of photoinduction of electron transfer upon excitation of the lowest energy cobalt d–d transition decreases with increasing energy of the ligand π^* orbitals (Figure 4). Disruption of π conjugation between metal centers, as with the allylacetate ligand, effectively blocks electron transfer. If quantum yields for competing photophysical processes (*e.g.*, internal conversion, intersystem crossing) of the excited dimers are negligible or constant with varying ligand structures, then the measured rates of Co(II) production are equivalent to relative rates for electron transfer in the dimers. The results suggest that electron transfer is mediated by the π-conjugated chain between metals with ligand π-antibonding orbitals being intimately involved in the process. Electron transfer is therefore consistent with operation of either superexchange or radial-ion mechanisms.[41] The large activation barrier to oxidation–reduction in the thermal reactions can be correspondingly understood, at least in part, by the necessity of providing a vacant acceptor orbital of appropriate symmetry for overlap with the π chain.[42] Restrictions placed upon the reactions arising from requirements of conservation of spin momenta, which are removed with d-d excitation of cobalt(III), may also be significant.[43] Preliminary measurements made on the thermal reaction of the $[\mathrm{(NH_3)_5Ru^{III}}$–acr–$\mathrm{Cu^{I}}]$ dimer indicate that electron transfer occurs at a substantial rate ($t_{1/2} \simeq 80$ sec, for reaction with excess Cu(I)). The driving force for electron transfer to the $\mathrm{(NH_3)_5Ru^{III}}$ moiety is nearly identical with that for Ro. but spin conservation and orbital symmetry requirements for electron transfer are adequately met by the ground-state $\mathrm{(NH_3)_5Ru^{III}}$ ion.

Discrimination with respect to the ligand is considerably reduced when the charge-transfer bands are irradiated, suggesting that the photoredox process is highly efficient. Particularly surprising is the observation that electron transfer remains effective when π conjugation between metal centers is removed. Electron transfer might occur in these cases by direct overlap of cobalt acceptor and ligand radical anion π^*-donor orbitals. Model building studies indicate that this suggestion is plausible. Alternatively, electron transfer might be intermolecular, *e.g.*, as in the reaction

$$\mathrm{RoL\cdot^{+} + RoL^{2+} \rightleftharpoons RoL^{2+} + Co^{2+} + L^{-}}$$

where the radical anion reduces an unexcited reactant ion. Quantitative study of the photochemistry of these systems is currently in progress.

It seems worthwhile to reiterate that this class of reactions offers considerable promise for resolution of the effects of reactant modification upon precursor complex stabilities and intrinsic electron transfer processes, a circumstance which has obtained previously only extremely infrequently.[4,5] Although reactions involving the Co(III) center are likely to be too sluggish to be generally useful without photoexcitation, cuprous complexes with other oxidant metal ions (*e.g.*, $\mathrm{(NH_3)_5Ru^{III}}$–) will almost certainly undergo oxidation–reduction at a convenient rate.

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[40] Oxidation potentials for the RoL ions are assumed to be approximately $E^0 = -0.33$ V, the value determined for the couple, $\mathrm{(NH_3)_5CoOH_2^{2+} \rightarrow RoOH_2^{3+} + e^-}$: R. G. Yalman, *Inorg. Chem.*, 1, 16 (1962).

[41] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 32 (1960).

[42] *Cf.* H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970, p 62 ff.

[43] *Cf.* W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966, Chapter 5.