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Formation Constants of Copper(I)–Olefin Complexes in Aqueous Solution

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A simple kinetic method has been applied to measure the formation constants of aqueous copper(I) with fumaronitrile, dimethyl fumarate, and fumaric and maleic acids. At 0.14 M ionic strength, the values of β_1 are $(0.85 \pm 0.02) \times 10^3$, $(6.1 \pm 0.1) \times 10^3$, $(7.3 \pm 0.1) \times 10^3$, and $(2.2 \pm 0.4) \times 10^3$ M^{-1}, respectively. The values for the last two olefins are compared to previous results. Values of β_1 for hydrogen maleate and β_2 for fumaronitrile also have been determined. A reanalysis of much earlier work has been done, and all the results are discussed in terms of the effect of substituents on the olefin on the β_1 values. The structure of bis(fumaronitrile)copper(I) nitrate also is reported. The nitrile is N-coordinated to copper(I), which has a distorted tetrahedral geometry, while the overall structure consists of macrocyclic Cu_6(fumaronitrile)$_6$ rings which extend in three dimensions.

Introduction

Formation constants of copper(I) complexes in water are somewhat difficult to measure because of the instability of aqueous copper(I) with respect to disproportionation and oxidation by dioxygen. The bulk of the previous work consists of early solubility studies of CuCl by Andrews and co-workers[1] and radiation chemistry to generate aqueous Cu(I) combined with spectrophotometry by Meyerstein and co-workers[2] and Buxton et al.[3] These methods either are tedious or require specialized equipment so that they have not been adopted more generally for systematic studies. A simple kinetic method has been developed recently[4] to measure formation constants of aqueous Cu(I) using standard spectophotometry. This method is applied here to the complexation of fumaric and maleic acids, for comparison to the other methods, and dimethyl fumarate and fumaronitrile, which are reported for the first time.

The interest in olefin ligands is in part related to the role of copper(I) in the ethylene receptors that are important in many phases of plant development.[5] There have been a number of model studies of copper(I)−olefin complexes[6] designed to mimic the biological receptor, and eventual comparison of these to the simple aqua system is of interest. Since the early work of Andrews and co-workers,[1] which predates the current picture of metal−olefin interactions, there has not been a consideration of the effects of substituents on the olefin on the strength of the complexation. The present and past results are considered from this perspective with a view to the implications about the importance of σ- and π-donation to the bonding.

Results

The kinetic method used is based on the variation with olefin concentration of the rate of reduction of azidopentaamminecobalt(III) by aqueous copper(I). It was found by Parker and Espenson[7] that this reaction is first order in the Cu(I) and Co(III) complex concentrations, and recently[4] this has been confirmed to be the case in the presence of acetonitrile. The essential reactions for the present study are shown in Scheme 1, where L is the olefin ligand.

If the complexation reactions (β_n) are assumed to be rapidly maintained equilibria and the concentration of L is

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(1) (a) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc*. **1948**, *70*, 3261. (b) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc*. **1949**, *71*, 1723. (c) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc*. **1949**, *71*, 2379. (d) Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc*. **1949**, *71*, 2381. (e) Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc*. **1949**, *71*, 3906.

(2) (a) Navon, N.; Masarwa, A.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **1997**, *261*, 29. (b) Meyerstein, D. *Inorg. Chem*. **1975**, *14*, 1716. (c) Saphier, M.; Burg, A.; Sheps, S.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans*. **1999**, 1845,

(3) Buxton, G. V.; Green, J. C.; Sellers, R. M. *J. Chem. Soc., Dalton Trans*. **1976**, 2160.

(4) Kamau, P.; Jordan, R. B. *Inorg. Chem*. **2001**, *40*, 3879.

(5) Abeles, F. B.; Morgan, P. W.; Selveit, M. E. *Ethylene in Plant Biology*, 2nd ed.; Academic Press: San Diego, 1994.

(6) Hirsch, J.; George, S. D.; Solomon, E. I.; Hedman, B.; Hodgson, K. O.; Burstyn, J. N. *Inorg. Chem*. **2001**, *40*, 2439, and references therein.

(7) Parker; Espenson, J. H. *J. Am. Chem. Soc*. **1969**, *91*, 1968.

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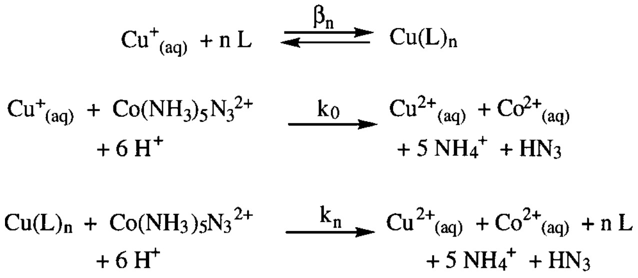
Scheme 1



$$\mathrm{Cu^{+}_{(aq)} + n\,L \underset{}{\overset{\beta_n}{\rightleftharpoons}} Cu(L)_n}$$

$$\mathrm{Cu^{+}_{(aq)} + Co(NH_3)_5N_3^{2+} + 6\,H^+ \xrightarrow{k_0} Cu^{2+}_{(aq)} + Co^{2+}_{(aq)} + 5\,NH_4^+ + HN_3}$$

$$\mathrm{Cu(L)_n + Co(NH_3)_5N_3^{2+} + 6\,H^+ \xrightarrow{k_n} Cu^{2+}_{(aq)} + Co^{2+}_{(aq)} + n\,L + 5\,NH_4^+ + HN_3}$$

much larger than that of copper(I), then the rate of disappearance of the cobalt(III) complex is given by

$$-\frac{d[\mathrm{Co(III)}]}{dt} = \frac{k_0 + \sum k_n\beta_n[\mathrm{L}]_n}{1 + \sum \beta_n[\mathrm{L}]^n}[\mathrm{Co(III)}][\mathrm{Co(I)}]_{\mathrm{tot.}} \quad (1)$$

$$-\frac{d[\mathrm{Co(III)}]}{dt} = k_{2\mathrm{obsd}}[\mathrm{Co(III)}][\mathrm{Cu(I)}]_{\mathrm{tot.}} \quad (2)$$

where $[\mathrm{Cu(I)}]_{\mathrm{tot.}} = [\mathrm{Cu}^+_{(\mathrm{aq})}] + \Sigma[\mathrm{Cu(L)}_n]$. Comparison of eqs 1 and 2 shows that $k_{2\mathrm{obsd}}$ is a function of [L] and the β_n values, and the variation of $k_{2\mathrm{obsd}}$ with [L] can be used to evaluate β_n. To simplify the elaboration of the analysis, it can be noted that, for a number of the systems studied here, k_0 is the dominant term in the numerator of eq 1 and $n \leq 2$. Then

$$k_{2\mathrm{obsd}} = \frac{k_0}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2} \quad (3)$$

Since k_0 is known independently,[4] eq 3 can be rearranged to

$$\left(\frac{k_0}{k_{2\mathrm{obsd}}} - 1\right) = \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 \quad (4)$$

If there is no bis-complex formation, then a plot of the left hand side of eq 4 versus [L] will be linear with a slope of β_1. If there is bis-complex formation, then the plot will show upward curvature. In this case, dividing both sides of eq 4 by [L] gives a new function which can be plotted versus [L] to give β_1 as the intercept and β_2 as the slope. If the plot shows downward curvature, the implication is that the $k_n\beta_n$ terms in eq 2 are contributing. For the systems described below, eq 4 is the starting point for the analysis, and the model is expanded only when necessary. In the final analysis, the data were fitted by nonlinear least squares to the approriate model indicated by the graphical analysis.

For the β_n determinations here, the ionic strength is 0.141 M, the rate of disappearance of $\mathrm{Co(NH_3)_5N_3^{2+}}$ was monitored at 516 nm, and the previously determined[4] value of $k_0 = 1.42 \times 10^3$ M^{-1} s^{-1} has been used.

Fumaric Acid and Dimethyl Fumarate. These systems are described together because the results are quite similar. Fumaric acid (pK_{a1} = 3.08)[8] is essentially undissociated under the experimental conditions of 0.033 and 0.109 M H$^+$, and the lack of an [H$^+$] dependence of $k_{2\mathrm{obsd}}$ confirms that complexation by the hydrogen fumarate anion is not detectable under these conditions. For the fumaric acid system, 24 kinetic runs were used, covering the following range of conditions: [L], 0.50−21 mM; $[\mathrm{Cu(I)}]_{\mathrm{tot.}}$, 0.13−1.13 mM; [Co(III)], 0.19−1.34 mM. For dimethyl fumarate, 16 kinetic runs were used and the analogous ranges are as follows: 0.5−6.0, 0.06−0.328, and 0.334−0.359 mM, respectively. The full data sets are tabulated in the Supporting Information. The rate is first order in $[\mathrm{Cu(I)}]_{\mathrm{tot.}}$ and [Co(III)] and independent of [H$^+$] (0.033, 0.109, and 0.140 M). $k_{2\mathrm{obsd}}$ decreases monotonicaly as [L] increases, as expected from eq 3.

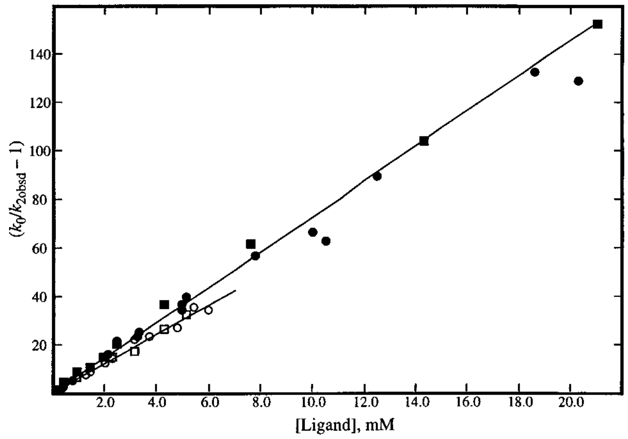


Figure 1. Variation of $(k_0/k_{2\mathrm{obsd}} - 1)$ with olefin concentration, for fumaric acid ([H$^+$] = 0.109 (■) or 0.033 M (●)) and dimethyl fumarate ([H$^+$] = 0.109 (□) or 0.033 M (○)).

The plots in Figure 1 show that these systems conform to eq 4, and their linearity shows that β_2 is not making a detectable contribution. Least-squares analysis gives values for β_1 of (7.3 ± 0.15) × 10^3 and (6.1 ± 0.1) × 10^3 M^{-1} for fumaric acid and dimethyl fumarate, respectively.

Fumaronitrile. This system introduces two new features, namely, the formation of a bis-complex and the crystal structure of a copper(I)−fumaronitrile complex, which is described in the next section. For this system, 34 kinetic runs were used, covering the following range of conditions: [L], 6.67−130 mM; $[\mathrm{Cu(I)}]_{\mathrm{tot.}}$, 0.082−0.475 mM; [Co(III)], 0.34−0.675 mM. The reaction rate is first order in $[\mathrm{Cu(I)}]_{\mathrm{tot.}}$ and [Co(III)] and independent of [H$^+$] (0.033, 0.109, and 0.140 M). The full data set is given in the Supporting Information.

The plot in Figure 2 shows upward curvature from the dashed line obtained by extrapolation of the results at low fumaronitrile concentrations. This behavior is consistent with eq 4 if the $\beta_2[\mathrm{L}]^2$ term is contributing. Least-squares analysis gives values for β_1 and β_2 of (8.5 ± 0.2) × 10^2 and (2.0 ± 0.4) × 10^3 M^{-2}, respectively. The curve in Figure 2 is calculated with these parameters. The second stepwise formation constant is given by $K_2 = \beta_2/\beta_1 = 2.4$ M^{-1} and is noteably 350 times smaller than K_1 (=β_1).

Bis(fumaronitrile)copper(I) Nitrate Crystal Stucture. Full details of the structure determination with bond lengths and angles are given in the Supporting Information. The most notable feature is that the copper(I) is coordinated to the

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[8] Smith, R. M.; Martell, A. E.; Motekaitis, R. *NIST Critically Selected Stability Constants of Metal Complexes Database*, Version 2; National Institute of Standards and Technology: Washington, DC, 1995.

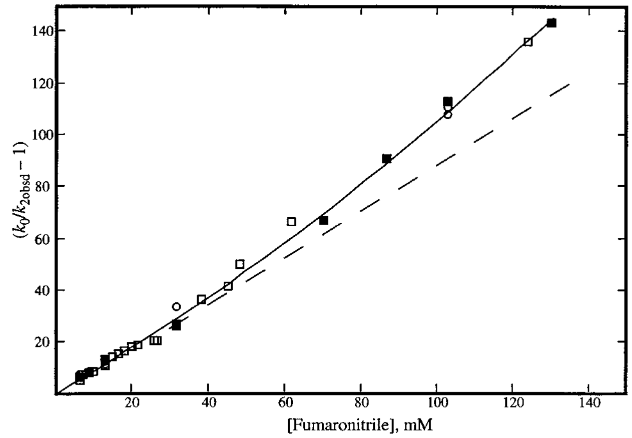

Figure 2. Variation of (k_0/k_{2obsd} − 1) with fumaronitrile concentration ($[H^+]$ = 0.140 (□), 0.109 (■), or 0.033 M (○)). The dashed line is predicted for monofumaronitrile complex formation, by extrapolation from [fumaronitrile] ≤ 20 mM.

N-atom of the nitrile. The structure consists of macrocyclic Cu_6(fumaronitrile)$_6$ rings which extend in three dimensions to form an open structure into which the nitrate ions are packed. Each copper(I) is coordinated to four monodentate fumaronitriles, while each fumaronitrile is coordinated to two copper(I) ions.

The coordination geometry is a distorted tetrahedron, as observed in the analogous succinonitrile complex.[9] The N−Cu−N bond angles range from 103.8 to 118.9° with an average Cu−N bond length of 1.97 Å. The nitrile group is not linearly coordinated to Cu; two C−N−Cu angles are 158.3°, and two are 168.4°. The NC and C═C bond lengths have normal average values of 1.15 and 1.31 Å, respectively. The nitrate ion appears to be uncoordinated since the shortest Cu−O distance is 4.22 Å.

Maleic Acid. This acid differs from fumaric in having a cis-arrangement of the carboxylate groups. One consequence of this is that maleic acid is a much stronger acid (pK_{a1} = 1.75)[8] because the anion is stabilized by hydrogen bonding. As a result, there will be significant amounts of the anion (HL^-) and the acid (H_2L) present under the acidity conditions of this study. Because of this dissociation, the ligand also may contribute significantly to the total H^+ concentration and this has been taken into account during the analysis. Because it can form bidentate chelates, maleic acid is a much better complexing agent than fumaric acid and does complex with copper(II). The formation constants for the copper(II)−maleic acid system are known,[8] and calculations indicate that insignificant amounts ($\leq 3 \times 10^{-8}$ M) of the ligand are complexed under the moderately high acidity and low total copper concentrations of these experiments.

For the kinetic study, 24 runs were used, covering the following range of conditions: $[H_2L]_{tot.}$, 0.50−83.8 mM; $[Cu(I)]_{tot.}$, 0.139−0.275 mM; [Co(III)], 0.34−0.645 mM. Runs also were done in 3.30×10^{-2} and 10.9×10^{-2} M $HClO_4$. The rate law is the same as for the previous systems, except that k_{2obsd} does depend on $[H^+]$ and is smaller at the lower $[H^+]$. This is what one would expect if the anion HL^- is complexing with copper(I).

To account for complexation by both the acid (H_2L) and the anion (HL^-), their formation constants will be designated β_{12} and β_{11}, respectively. The species concentrations can be expressed in terms of the total Cu(I) ($[Cu(I)]_{tot.} = [Cu^+] + [Cu(H_2L)^+] + [Cu(HL)]$) and the total ligand ($[H_2L]_{tot.} = [H_2L] + [HL^-]$) and the final hydrogen ion concentration $[H^+]$, which includes H^+ from $HClO_4$ and ionization of H_2L. Then the copper(I) species concentrations are given by

$$[Cu^+] = \frac{[Cu(I)]_{tot.}}{1 + (\beta_{12}[H^+] + \beta_{11}K_{a1})(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}} \quad (5)$$

$$[Cu(H_2L)^+] = \frac{\beta_{12}[H^+](K_{a1} + [H^+])^{-1}[H_2L]_{tot.}[Cu(I)]_{tot.}}{1 + (\beta_{12}[H^+] + \beta_{11}K_{a1})(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}} \quad (6)$$

$$[Cu(HL)] = \frac{\beta_{11}K_{a1}(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}[Cu(I)]_{tot.}}{1 + (\beta_{12}[H^+] + \beta_{11}K_{a1})(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}} \quad (7)$$

If all of the Cu(I) species act as reducing agents, then the rate of disappearance of the Co(III) complex is given by

$$-\frac{d[Co(III)]}{dt} = (k_0[Cu^+] + k_{12}[Cu(H_2L)^+] + k_{11}[Cu(HL)])[Co(III)] \quad (8)$$

and substitution for the species concentrations gives the second-order rate constant as

$$k_{2obsd} = \frac{\{k_0 + (k_{12}\beta_{12}[H^+] + k_{11}\beta_{11}K_{a1})(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}\}}{1 + (\beta_{12}[H^+] + \beta_{11}K_{a1})(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}} \quad (9)$$

If this system follows the pattern of the others, then the k_{12} and k_{11} terms will be small relative to k_0, and the expression simplifies to

$$k_{2obsd} = \frac{k_0}{1 + (\beta_{12}[H^+] + \beta_{11}K_{a1})(K_{a1} + [H^+])^{-1}[H_2L]_{tot.}} \quad (10)$$

Unfortunately, this function cannot be rearranged to permit a graphical presentation of all of the data because of the two independent variables, $[H^+]$ and $[H_2L]_{tot.}$. However, several runs at different $[H_2L]_{tot.}$ happen to have been done at reasonably constant $[H^+]$ of (3.30−3.60) × 10^{-2} and (10.9−11.6) × 10^{-2} M. If eq 10 is rearranged, as was done to obtain eq 4, then the plots in Figure 3 should be linear with a zero intercept and a slope of $\beta_{12}[H^+] + \beta_{11}K_{a1}$, and the slope should be larger for larger $[H^+]$ if the β_{12} term is significant. Clearly the results conform to the predictions and provide preliminary values for β_{12} and β_{11} of 2.3×10^3 and 18×10^3 M^{-1}, respectively.

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[9] Blount, J. F.; Freeman, H. C.; Hemmerich, P.; Sigwart, C. *Acta Crystallogr.* **1969**, *B25*, 1518.

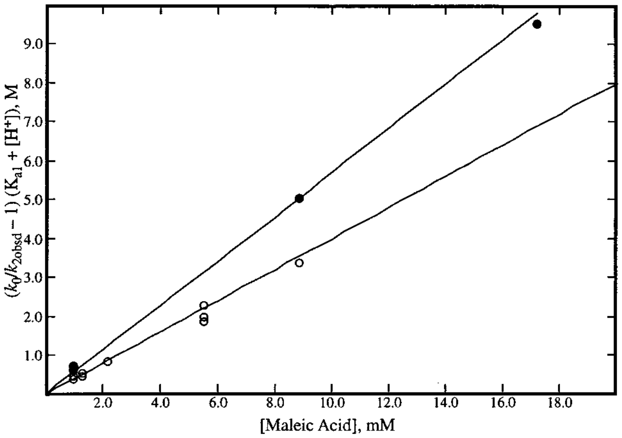

Figure 3. Variation of ($k_0/k_{2obsd} - 1$) with maleic acid concentration for 0.113 ± 0.004 M H^+ (●) and 0.0345 ± 0.015 M H^+ (○). The actual [H^+] is slightly variable because of the ionization of maleic acid.

The full data set was analyzed by least-squares fitting. It was noted that fitting to eq 10 consistently underestimated the values of k_{2obsd} by ∼25% for the higher [H^+] and $[H_2L]_{tot.}$. This systematic deviation can be overcome, and the overall standard error of the fit improved by a factor of 1.8 if either the $k_{12}\beta_{12}$ and/or $k_{11}\beta_{11}K_{a1}$ terms in the numerator of eq 9 are retained. Fortunately, these refinements change the best-fit values of β_{12} and β_{11} by less than the standard error on the parameter, and the results give $\beta_{12} = (2.2 \pm 0.4) \times 10^3$ M^{-1} and $\beta_{11} = (17.9 \pm 0.9) \times 10^3$ M^{-1}.

The above analysis also can be used to provide estimates of k_{12} or k_{11} of 5.6 and 2.1 M^{-1} s^{-1}, respectively. These values are $\sim 10^3$ times smaller than k_0, and a similar factor was determined[4] for the reduction rate constant for $Cu(NCCH_3)^+$, but there is no clear rationale for suggesting whether k_{12} or k_{11} or both are contributing in the maleic acid system.

Aromatic System. There is somewhat conflicting information in the literature on the complexation of a benzene ring system by aqueous copper(I), as described more fully in Discussion. Two such ligands have been investigated here, benzoic acid and *p*-toluenesulfonate. The latter was chosen because of its high solubility in water. The results may be briefly stated because k_{2obsd} was found to be almost indistinguishable from k_0 for concentrations of 0.39−9.8 mM benzoic acid and 2.06 and 20.6 mM *p*-toluenesulfonate in 3.30×10^{-2} M $HClO_4$. Therefore, no significant complexation was detected, and only upper limits on β_1 of $\leq 3 \times 10^2$ and ≤ 0.8 M^{-1} can be given for benzoic acid and *p*-toluenesulfonate, respectively.

Another explanation of these observations is that $Cu^+_{(aq)}$ and its complexes with aromatic ligands happen to have almost the same rate constants for reduction of $Co(NH_3)_5N_3^{2+}$. Two experiments were done to check for comproportionation, driven by complexation, in these systems. A nearly saturated solution of benzoic acid (6.0 mM) and 20 mM copper(II) nitrate was placed over copper metal, deoxygenated, and allowed to stand for 24 h. Then a 6 mL aliquot of this solution was added to an equal volume of a deoxygenated solution containing 0.60 mM $Co(NH_3)_5N_3^{2+}$ and 6.0 M benzoic acid in a 5.0 cm spectrophotometer cell. The absorbance at 516 nm was recorded immediately after mixing and was found to be constant for 10 min and somewhat lower than that of a blank solution containing $Co(NH_3)_5N_3^{2+}$, benzoic acid, and copper(II) nitrate at the same concentrations. The absorbance change corresponds to a concentration of Cu(I) in the stock solution of ∼0.1 mM, similar to the 0.11 mM expected from simple comproportionation of a 20 mM Cu(II)/Cu mixture. If $\beta_1 \geq 10^2$ M^{-1}, then this concentration would be $\geq 2.0 \times 10^{-4}$ M. As a qualitative check, a solution containing 0.25 M *p*-toluenesulfonate, 0.045 M copper(II) nitrate, and 0.033 M $HClO_4$ was placed over copper metal and deoxygenated. After several days, there was no evidence of the disappearance of the blue color of copper(II) nor formation of the yellow color that is typical of the other olefin complexes. Blank tests indicate that a 25% change in the Cu(II) concentration would be evident to the eye, so that the lack of color change requires that $\beta_1 < 3 \times 10^2$ M^{-1} for *p*-toluenesulfonate. For both systems, these results are consistent with the upper limits on β_1 from the kinetic studies but are not consistent with β_1 values in the range of 104 M^{-1} for benzoic acid and related systems.[2c]

Reanalysis of Previous Results. Many years ago, Andrews and co-workers[1] published a series of papers on the complexation of copper(I) by a number of olefins. They studied the solubility of CuCl(s) as a function of the concentrations of olefin, chloride ion, and H^+. The total copper(I) in solution was determined, and the system analyzed with the assumptions that the species in solution were $Cu(olefin)^+$, Cu(Cl)(olefin), and $Cu(Cl)^{2-}$. The monoanion was included for the maleic acid system. The method of analysis for extracting the formation constants was not described, but it used known values of $K_{sp} = 1.85 \times 10^{-7}$ M^2 for CuCl(s) and $\beta_2 = 3.5 \times 10^5$ M^{-2} for $Cu(Cl)^{2-}$ at 0.10 M ionic strength. The current reanalysis has simply involved expansion of the model to include[10] $CuCl_{(aq)}$ and $CuCl_3^{2-}$ and least-squares fitting of the data of Andrews et al. to obtain best-fit values of the formation constants and their error limits. In general, there are only minor changes from the original values. The results are tabulated in the Supporting Information.

Discussion

The structures of the olefins that have been studied by various workers are shown in Chart 1. The results from this study and the published results on the fumaric and maleic acid systems are summarized in Table 1. The results of the current study and that of Meyerstein and co-workers[2a] generally are in good agreement. The values of Andrews and co-workers1 are somewhat different but generally within the 95% confidence limits, which are typically ∼3 times larger than the standard error values given in Table 1. The numerical analysis of Andrews' data also is more complicated because it involves a determination of the formation constants of both $Cu(olefin)^+$ and Cu(olefin)(Cl).

It is interesting to note that, if the formation constants for Cu(olefin)(Cl) are expressed as β_{1Cl} = [Cu(olefin)(Cl)]

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[10] Fritz, J. J. *J. Phys. Chem.* **1980**, *84*, 2241; **1981**, *85*, 840.

Chart 1

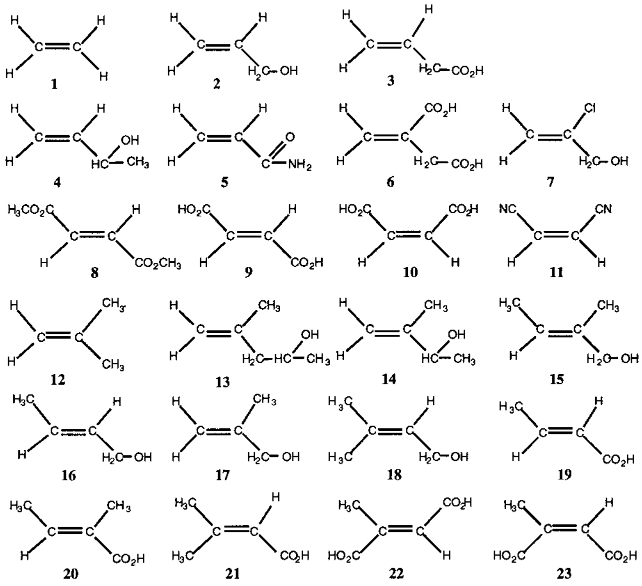

Table 1. Formation Constants for Aqueous Copper(I) with the Fumaric Acid and Derivatives, Maleic Acid, and Aromatic Systems

	$10^{-3} \times \beta_1$, M^{-1}			
olefin syst	H_2L	HL^-	L^{2-}	ref
fumaric acid	7.3 ± 0.15			this work
	7.3 ± 1.5	11.6 ± 2	15 ± 3	*a*
	9.2 (9.8 ± 1.0)^d			*b*
maleic acid	2.2 ± 0.35	17.9 ± 0.9		this work
	2.3 ± 0.5	11.5 ± 2.3	28 ± 6	*a*
	1.1 (1.5 ± 0.4)^d	20 (21 ± 2)^d		*c*
dimethyl fumarate	6.1 ± 0.1			this work
fumaronitrile	0.85 ± 0.02^e			this work
benzoic acid	$<3 \times 10^{2\,f}$			this work
p-toluenesulfonate	$<0.8^{\,f}$			this work

[a] Reference 2a. [b] Reference 1d. [c] Reference 1c. [d] Results of least-squares analysis of the published data. [e] Fumaronitrile also has $\beta 2 = (2.0 \pm 0.4) \times 10^3$ M^{-2}. [f] No detectable complexation from kinetic studies.

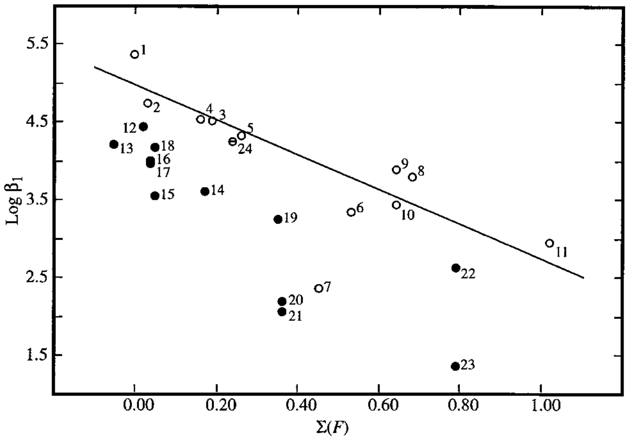

Figure 4. Variation of log β_1 with the sum of the inductive parameters (*F*) for the substituents on the olefin: with CH_3 substituents (●), hydrogen maleate anion (⊖), and all other substituents (○). The olefin numbering is given in Chart 1.

[CuCl]$^{-1}$[olefin]$^{-1}$, then the ratio β_1/β_{1Cl} falls in the rather narrow range of 13−27 for 12 of the 17 acids and alcohols studied by Andrews. This ratio is ∼10 times smaller (2.4−3.4) for tiglic (**20**), dimethylacrylic (**21**), and maleic acids (**10**), and 10 times larger (194) for hydrogen maleate. It appears generally that the added chloride ligand disfavors olefin complexation; the negative charge on the olefin may enhance the effect for hydrogen maleate. However, the orgin of the varying magnitude in the other cases remains an open question.

The general influence on β_1 of substituents on the olefin can be represented as a plot of the sum of the inductive substituent constants (*F*),[11] as shown in Figure 4, where the numbering system is given in Chart 1. There is a general trend to smaller values of β_1 for more electron-withdrawing substituents; possible reasons for some of the deviations from this trend are discussed below. Within the framework of the Dewar−Chatt−Duncanson[12] model for olefin bonding to a metal, this trend suggests that σ-donation from the olefin is more important than π-back-bonding from the copper(I). This also is consistent with the observation above that a chloride ligand disfavors olefin complexation. Substituent effect correlations also have been noted for olefin complexation by Ag$^+$,[13] Ni(P(O-*o*-tolyl)$_3$)$_2$ and Ni(CN-*tert*-butyl)$_2$.[14] The trend with Ag$^+$ is the same as that found here, and σ-donation is taken to dominate, but the Ni(0) systems show the opposite trend with more electron-withdrawing substituents giving stronger complexation, and π-back-bonding appears to be dominant.

NMR chemical shifts of the ^{1}H and ^{13}C nuclei also have been used to assess the σ- and π-contributions to the bonding. For cyclic monoolefins, the downfield ^{1}H shifts observed by Salmon and Kochi,[15] with copper(I) trifluoromethanesulfonate, and Baum et al.,[16] with (hexafluoroacetylacetonate)copper(I), were interpreted as consistent with important σ-donation from the olefin. However, the same copper(I) complex gave upfield shifts with norbornadiene ligands having a weakly complexing 7-*tert*-butoxyl substituent.[17] With analogous polyolefins, Salmon and Kochi observed upfield ^{1}H shifts, but the nature of the species is somewhat uncertain. Clearly the ^{1}H shifts reflect subtle changes in the ligand but are difficult to interpret in terms of the relative importance of the σ- and π-donation to the strength of the bonding.

The published theoretical analyses of the importance of π-back-bonding in the copper(I)−ethylene system are somewhat equivocal. The initial study by Ziegler and Rauk[18] suggested that π-back-bonding makes a significant contribution, but later work[19] indicated a negligible contribution. More recently, Budzelaar et al.[20] found, in agreement with

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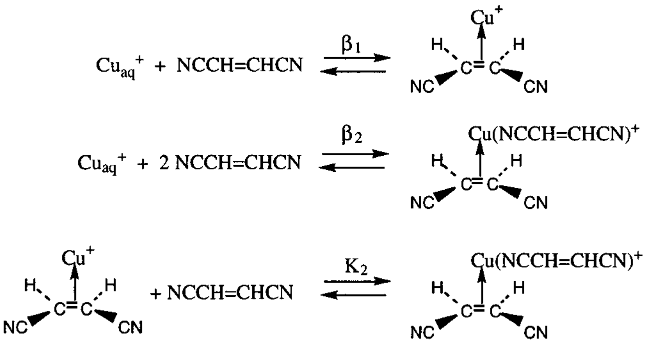
Ziegler and Rauk, that π-back-bonding contributes about a third of the total interaction energy, and Huang et al.[21] have predicted back-donation of electron density is about double σ-donation in (X)Cu(olefin) systems (X = F^-, Cl^-, Br^-, I^-; olefin = ethylene or propylene). The overall strength of the metal−olefin interaction increases with the electronegativity of the halide, and this seems to indicate an important contribution of σ-donation to the bond strength.

In Figure 4, the ligands are divided into two groups, with the closed circles being those with at least one methyl substituent on an olefinic carbon. The latter ligands constitute the majority of those that do not fit the trend in that their β_1 values are consistently too small. This effect was originally noted by Andrews and co-workers who attributed it to steric effects. However, the current picture[12] of side-on binding of an olefin to a metal seems to obviate any significant steric problem between a methyl group and ancilliary H_2O ligands. Tolman[14] noted the destabilization by alkyl substitution in the Ag^+, $Ni(P(O\text{-}o\text{-tolyl})_3)_2$, and Rh(acac)[22] systems, and the magnitude of the effect seems far beyond that expected from substituent-effect parameters. In the $Ni(P(O\text{-}o\text{-tolyl})_3)_2$ and Rh(acac) systems, electron-donating substituents disfavor complexation so that alkyl substitution at least followed the general trend. However, with Ag^+ and Cu^+, the electron-donating alkyl substituents are expected to enhance complexation, but the opposite is observed. A possible explanation may lie in the resistance, either steric or electronic, to the bending back of the substituents on the olefin in the complex.

Another explanation might invoke the observation[23] that the metal shifts away from the substituted carbon for asymmetrically substituted olefins, whether the substituent is a π-donor or π-acceptor. Hoffmann et al.[24] have suggested that this can be explained by the effect of the different donor types on the energies and orbital coefficients of the π- and π^*-orbitals, and this explanation seems to have been rediscovered as part of the DFT calculations[21] on the (X)-Cu(olefin) systems. It is not qualitatively obvious whether the lengthening of one bond and shortening of the other will strengthen or weaken the overall metal−olefin interaction, relative to the symmetrical olefin. The DFT calculations suggest that ΔH is ~3 kcal mol^{-1} more favorable for propylene than for ethylene bonding to CuX. The structures of two allylammonium π-complexes of copper(I)[25] show that the Cu−C bond length differences are in the normal direction but small (~0.02 Å). In any case, asymmetrical substitution is not an entirely viable explanation because several asymmetrical olefins (**2**−**5**) seem to fit the correlation in Figure 4.

Scheme 2



One olefin that does not have methyl substituents, β-chloroallyl alcohol (**7**), also does not fit the correlation. Navon et al.[26] have noted that aqueous copper(I) is oxidized by trichloroacetic acid, and an analogous reaction is possible with **7**, but may have gone unnoticed by Andrews and co-workers. It also should be noted that **7** and another major deviant, citraconic acid (**23**), are the only systems for which Andrews and co-workers made only the minimum number of measurements (2) to characterize the system. It is remarkable that the introduction of one methyl substituent on maleic acid to give **23** should reduce β_1 by a factor of 10^2. Precipitation of copper(I) citraconate is a possible complication.

As a caution about the use of substituent effect correlations in this area, it should be noted that the β_1 values for olefin complexation by $Cu(phen)^+$ in 0.3 M acetonitrile/ethanol do not show a simple correlation.[27] The values generally decrease with increasing substitution of $-CO_2H$, $-CO_2CH_3$, $-COCH_3$, $-CN$, and $-CH_3$ groups, as observed here, but increase as $-CN$ is replaced by $(-Cl)_3$ and $(-Cl)_4$.

The results in Figure 4 provide some guidance for the mode of coordination of fumaronitrile (**11**). The system fits the correlation for η^2-C=C coordination, but the solid has η^1-N coordination of the ligand. This also is the only ligand that gives a detectable bis-complex (β_2). These observations can be rationalized if the formation constants are assigned as shown in Scheme 2.

The value of $K_2 = 2.3\ M^{-1}$ is somewhat smaller than the $K_2 = 23\ M^{-1}$ for $Cu(NCCH_3)^{2+}$,[4] as might be expected if the uncoordinated nitrile group makes fumaronitrile a poorer base than acetonitrile. If the opposite assignment is made, then the β_1 for N-coordination of fumaronitrile would be ~2 times larger than the β_1 of $4.3 \times 10^2\ M^{-1}$ for acetonitrile,[4] and β_1/K_2 would be 370 versus 18 for acetonitrile.

The crystal structure also emphasizes the danger of inferring coordination mode from color in these systems. Solutions of copper(I)−olefins are often pale yellow, especially with electron-withdrawing substituents ($-CN$, CO_2H, CO_2R) on the olefin, but simple copper(I) solutions of

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saturated nitriles are colorless. In the solid state, various salts of $Cu(NCCH_3)^{4+}$ are colorless. The perchlorate salt of the fumaronitrile complex reported here also is colorless, although it is precipitated from a yellow solution. But the nitrate salts of the bis-complexes of fumaronitrile and its saturated analogue, succinonitrile,[28] are yellow, but have N-coordination. The allylammonium bis-sulfamate[25a] is a colorless molecular crystal, while the chloro-bridged solid[25b] is an extended network, but also is colorless. It seems that the colors of the solids are more a property of the overall lattice, including the anion, than of the monomeric copper(I)−ligand system.

The failure to detect complexation of aqueous copper(I) with the benzene rings of benzoic acid and the *p*-toluenesulfonate ion is at variance with the claim of Meyerstein and co-workers[2c] that analogous systems have β_1 values of $\sim 10^4$ M. The only other equilibrium study of an aqueous copper(I)−-aromatic system is the report of Hurst and Lane[29] with benzoatopentaamminecobalt(III). These authors failed to detect any complexation and derived an upper limit of $\beta_1 \leq 10^2\ M^{-1}$. For comparison, the analogous hydrogen fumarate complex has $\beta_1 = 4.4 \times 10^3\ M^{-1}$.[29] Several η^2-arene complexes of copper(I) have been isolated from noncoordinating solvents with ancillary trifluoromethanesulfonate,[30,31] chloride,[32] or tridentate macrocyclic ligands.[33,34] The trifluoromethanesulfonate species is thermally stable to 120 °C, although it does react in air; the benzene is readily replaced by other olefins, even in benzene. For the others, the arene seems to be rather prone to dissociation of the arene ligand from the solid or fluxionally. For several $(S)_2$-coordinating diphenylborato ligands, Ohrenburg et al.[35] have characterized the monomeric bis-acetonitrile complex and a tetramer with phenyl group coordination. The latter is readily replaced by acetonitrile to yield the monomer. The Cu−C bond lengths in the arene complexes (>2.2 Å) tend to be longer than those for olefins (∼2.0 Å). In summary, these observations suggest that benzene coordination to copper(I) is weaker than that of acetonitrile and simple olefins, but do not provide a conclusive indication of how benzene might compete with water as a ligand.

Experimental Section

Materials. Fumaric acid (Matheson, Coeman and Bell), maleic acid (Eastman), dimethylfumarate (Aldrich), and copper(II) nitrate trihydrate (Allied Chemical) were used as received. Fumaronitrile (Fluka) was purified by recrystallization from benzene.[36] Pentaammineazidocobalt(III) nitrate was prepared and characterized as described previously.[4]

Stock solutions of copper(II) nitrate were prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ in water and standardized by reaction with excess KI and back-titration with sodium thiosulfate. Stock solutions of $HClO_4$, HNO_3, and $NaClO_4$ were prepared and standardized as described previously, while $NaNO_3$ solutions were made from weighed amounts of the solid. Stock solutions of fumaric acid (4.00×10^{-2} M), maleic acid (0.200 M), dimethylfumarate (1.00×10^{-2} M), and fumaronitrile (0.200 M) were prepared from weighed amounts of the solids.

The solutions of the copper(I)−olefin complexes were prepared by comproportionation of copper(II) and copper metal in the presence of the olefin (L), according to the following reactions.

$$Cu^{2+}_{(aq)} + Cu_{(s)} \rightleftarrows 2Cu^{+}_{(aq)} \qquad K_{com} = 6 \times 10^{-7} \tag{11}$$

$$2Cu^{+}_{(aq)} + 2L \rightleftarrows 2Cu(L)^{+}_{(aq)} \qquad \beta_1^{\,2} \tag{12}$$

$$Cu^{2+}_{(aq)} + Cu_{(s)} + 2L \rightleftarrows 2Cu(L)^{+}_{(aq)} \qquad K = K_{com}\beta_1^{\,2} \tag{13}$$

As long as $\beta_1 > 4 \times 10^2\ M^{-1}$, reaction 13 will be spontaneous and will be a convenient source for significant concentrations of the copper(I)−olefin complex. These solutions were prepared daily by mixing appropriate volumes of the stock olefin and copper(II) solutions in an Erlenmeyer flask containing some copper foil. The flask was fitted with a serum cap and deoxygenated for ∼2 h with argon. The solution starts to change from pale blue to yellow in a few minutes, and the reaction is complete (on the basis of Cu(I) analysis with $Co(NH_3)_5N_3^{2+}$) in 2−3 h, except with fumaronitrile where 6−8 h was required.

For the benzoic acid and *p*-toluenesulfonate studies, comproportionation did not seem to occur, so the aqueous copper(I) was generated by reduction with aqueous chromium(II), as described by Espenson and Shaw.[37] This produces metastable solutions of copper(I) that were mixed with a solution of appropriate concentrations of the arene and $Co(NH_3)_5N_3^{2+}$ on a stopped-flow system.

$Cu(O_2CCHCHCO_2H)$. A 20 mL aliquot of 0.040 M aqueous fumaric acid was added to 5.0 mL of 4.48 mM copper(II) nitrate in contact with copper foil. The vessel was closed with a serum cap and deoxygenated with argon. After ∼3 h, a fine yellow powder began to precipitate from the yellow solution, and the mixture was stored in a refrigerator (∼3 °C) overnight. Then the mixture was swirled, and the yellow suspension was decanted into a centrifuge tube. After centrifugation, the clear solution was decanted and the solid was washed with methanol and recentrifuged twice. The damp, intensely yellow solid was dried at 110 °C for 30 min. The dry product is stable in air, but slowly turns greenish-blue if moistened with water. It is insoluble in water, but slowly dissolves in acidic solution. The product was formulated on the basis of the elemental analysis. Anal. Calcd for $C_4H_3O_4Cu$: C, 26.90; H, 1.693; O, 26.69. Found: C, 26.69; H, 1.543; O, 36.26.

$Cu(NCCHCHCN) \cdot 1.5(ClO_4)$. A 20 mL aliquot of 0.20 M aqueous fumaronitrile was added to 5.0 mL of 8.96 mM copper(II) nitrate in contact with copper foil. The vessel was closed with a serum cap and deoxygenated for ∼6 h with argon. Then 20 mL of 2.46 M aqueous, deoxygenated $NaClO_4$ was added by syringe, and a fine white suspension of the product formed immediately. The suspension was decanted from the copper foil, and the product was collected by vacuum filtration on a 0.22 μm Millipore filter and dried by drawing air through the sample. The formulation of

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the product is based on the elemental analysis. Anal. Calcd for $C_6H_3N_3O_4ClCu$: C, 25.70; H, 0.918; N, 15.00. Found: C, 26.02; H, 1.079; N, 14.90.

$Cu(NCCHCHCN)_2(NO_3)$. An aqueous solution containing 30 mL of 0.20 M fumaronitrile, 10 mL of 44.8 mM copper(II) nitrate, and 10 mL of 0.139 M HNO_3 in contact with copper foil was deoxygenated with argon and allowed to react at ambient temperature for ∼5 h. The resulting yellow solution was placed in an ice bath in a refrigerator and, on standing overnight, yielded a yellow crystalline product. The product was collected by vacuum filtration and air-dried. A crystal was selected for the X-ray analysis. The formulation of the product is based on the elemental analysis and is consistent with the X-ray structure determination. Anal. Calcd for $C_8H_4N_5O_3Cu$: C, 34.40; H, 1.43; N, 24.80. Found: C, 33.38; H, 1.179; N, 24.16.

X-ray Structure. A yellow crystal, measuring 0.46 × 0.06 × 0.06 mm, was selected and mounted on a Bruker P4/RA/SMART 1000 CCD diffractometer[38] using Mo Kα radiation ($\lambda = 0.710\,73$ Å) at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 2852 reflections from the data collection. This yielded the following unit cell information: $a = 5.3667(5)$ Å, $b = 22.228(2)$ Å, $c = 8.8952(8)$ Å, $\beta = 98.7072°$, $V = 1048.90(17)$ Å^3, $Z = 4$, $\rho = 1.748$ g cm^3, and $\mu = 2.086$ mm^{-1}. The space group was determined to be $C2/c$ (No. 15). The data were corrected for absorption through use of the SADABS procedure. The structure was solved using direct methods (SHELXS-86)[39] and refinement was completed using the program SHELXL-93.[40] Hydrogen atom positions were assigned on the basis of the geometries of the attached carbon atoms and were given thermal positions 20% greater than those of the attached carbons. One set of fumaronitrile ligand atoms was found to be disordered in a 55:45 occupancy ratio, as indicated in the list of atomic coordinates. The final model refined to values of $R_1(F) = 0.0266$ (for 960 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0682$ (for all 1075 independent data). Complete data tables are given as a CIF file with the Supporting Information.

Kinetic Methods. The standard procedure was to place appropriate volumes of solutions of $(Co(NH_3)_5N_3)(NO_3)_2$, acid, and sodium salt into a 50 mm cylindrical optical cell, close the cell with a serum cap, and deoxygenate the contents with argon. Then the required volume of the copper(I)−olefin solution was introduced via syringe, and the reaction was monitored on a Cary 219 spectrophotometer. For the studies with benzoic acid and Tiron, a deoxygenated solution of the arene, $(Co(NH_3)_5N_3)(NO_3)_2$, acid, and sodium salt was mixed with an equal volume of aqueous copper(I), generated by chromium(II) reduction,[37] on aTriTech Dynamics stopped-flow system. The variation of absorbance at 516 nm (or 350 nm for benzoic acid) with time was analyzed as described below, to determine the second-order rate constant and the copper(I) concentration. The full details for each run are given in the Supporting Information.

The reactions were done under second-order conditions ([$Co(NH_3)_5N_3^{2+}$] > [Cu(I)]) so that the total change in absorbance and the known molar extinction coefficient of $Co(NH_3)_5N_3^{2+}$ (268 M^{-1} cm^{-1})[4] could be used to determine the actual Cu(I) concentration for each kinetic run. The concentration of olefin is always much greater than [Cu(I)]. The variation of absorbance (I) with time (t) was fitted by nonlinear least squares to the previously developed[4] eq 11,

$$I = I_\infty \Big/ \left[\left(\frac{I_0 - I_\infty}{I_0}\right) \exp\left\{-\frac{I_\infty k_{2\mathrm{obsd}}(t + t_\mathrm{m})}{\epsilon_\mathrm{A}}\right\} - 1\right] + I_\mathrm{b} \qquad (12)$$

where I_0 and I_∞ are the initial and final absorbances, ϵ_A is the molar extinction coefficient of $Co(NH_3)_5N_3^{2+}$, k_{2obsd} is the second-order rate constant, t_m is the mixing time, and I_b is the instrument blank absorbance. The I_0 was fixed on the basis of the known [$Co(NH_3)_5N_3^{2+}$] and ϵ_A. The least-squares analysis gave best-fit values of I_∞, k_{2obsd}, t_m, and I_b. In many cases, the latter two parameters were of minimal influence because t_m (∼15 s) was small compared to the overall reaction time, and I_b (∼0.02) was small compared to the overall absorbance change and the values were largely controlled by I_0.

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Supporting Information Available: Reagent concentrations and observed and calculated rate constants (Tables S1−S6) and X-ray crystallographic data, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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