

# Complex Formation Constants for the Aqueous Copper(I)–Acetonitrile System by a Simple General Method

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A simple spectrophotometric method for the evaluation of formation constants for aqueous copper(I) has been developed, based on the kinetics of reduction of  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$  complexes. The method has been applied to the aqueous copper(I)–acetonitrile system to determine the successive formation constants  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  as  $4.3 \times 10^2 \text{ M}^{-1}$ ,  $1.0 \times 10^4 \text{ M}^{-2}$ , and  $2.0 \times 10^4 \text{ M}^{-3}$ , respectively, in 0.14 M  $\text{NaClO}_4/\text{HClO}_4$  at  $21 \pm 1 \text{ }^\circ\text{C}$ .

## Introduction

It is well-known that, in aqueous solution, copper(I) disproportionates to copper(II) and copper metal. Many years ago<sup>1</sup> it was shown that, in acetonitrile, copper(II) and the metal comproportionate to copper(I). The implication of this observation that copper(I) is strongly complexed by acetonitrile was consistent with the even earlier preparation<sup>2</sup> of the stable salt  $[\text{Cu}(\text{NCCH}_3)_4](\text{NO}_3)$ . Now several such compounds have been prepared, with structural characterization of the  $\text{ClO}_4^-$ ,<sup>3</sup>  $\text{PF}_6^-$ ,<sup>4</sup> and  $\text{BF}_4^-$ <sup>5</sup> salts, and these serve as common starting materials<sup>6</sup> for copper(I) chemistry. In all of these compounds, the copper(I) is tetrahedrally coordinated to four acetonitrile ligands, bonded through the N-atom of the ligand. It is tempting to ascribe the stabilization of copper(I) by acetonitrile to the  $\pi$ -acidity of the ligand; however evidence for back-bonding in this and other copper(I) systems with  $\pi$ -acid ligands remains somewhat equivocal.<sup>7</sup>

Despite the importance of the copper(I)–acetonitrile system in copper(I) chemistry, there have been no reports that systematically determine the complex formation constants in aqueous acetonitrile. Various studies have reported estimates<sup>8</sup> or values for the bis and tris complexes<sup>9</sup> or relied on values from another study to obtain a new formation constant.<sup>10</sup> Cox et al.<sup>11</sup> have measured the reduction potentials in the  $\text{Cu}^{\text{II}}$  aqueous acetonitrile system, but these observations were not used to calculate formation constants.

There are inherent problems in determining formation constants for copper(I) complexes in aqueous or water-rich media. The first is the disproportionation problem mentioned above, although metastable aqueous solutions of copper(I) at millimolar concentrations can be made. A second complication is the air oxidation of copper(I) so that studies must be done anaerobically. Both of these factors make it somewhat difficult to routinely prepare solutions of known copper(I) concentration. A third limitation is that common spectrophotometric methods are not useful because copper(I) complexes with simple ligands tend to be at best weak absorbers in the near-ultraviolet and visible regions of the electronic spectrum. The earlier work on the copper(I)–acetonitrile system used electrochemical methods,<sup>8,9</sup> and more recently Zuberbühler and co-workers<sup>10</sup> have used a kinetic method based on scavenging of copper(I) by dioxygen, monitored by an oxygen-sensitive electrode.

A major goal of this study was to develop a convenient method for the determination of complex formation constants with copper(I). This has been done by using pentaamminecobalt(III) complexes as scavengers for copper(I) and monitoring the rate of disappearance of the cobalt(III) complex in the visible or near-ultraviolet region using conventional spectrophotometry. Parker and Espenson<sup>12</sup> found that various  $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{X}$  complexes are reduced by aqueous copper(I) with rate constants that vary over 10 orders of magnitude, depending on the nature of the heteroligand, X. For present purposes, this has the advantage that one can select the X ligand to give a conveniently measurable rate. In this study, the complexes  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  and  $(\text{NH}_3)_5\text{CoBr}^{2+}$  have been used. Various salts of the  $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{X}$  complexes are easily prepared, and their solutions are reasonably stable in neutral to acidic conditions. Because of their stability, the extinction coefficients of the cobalt(III) complexes can be readily determined and the total absorbance change can be used as a measure of the total copper(I) concentration under conditions where  $[\text{Co}(\text{III})] > [\text{Cu}(\text{I})]$ . In essence, the method involves the determination of the second-order rate constant ( $k_2$ ) for the reduction of the cobalt(III) complex at varying concentrations of the ligand (acetonitrile in the present case) and analyzing the variation in  $k_2$  in terms of the copper(I) complexes present in order to determine their formation constants.

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## Experimental Section

**Materials.** Acetonitrile (specific gravity 0.777 g cm<sup>-3</sup>, 99.5%, 0.3% water, BDH), copper foil (Matheson Coleman and Bell), silver nitrate (Johnson, Matthey and Mallory Ltd.), copper(II) nitrate trihydrate (Fisher Scientific), 30 mesh zinc granules (Fisher Scientific), cobalt(II) sulfate heptahydrate (Matheson, Coleman and Bell), cobalt(II) nitrate hexahydrate (Mallinckrodt), sodium azide (BDH), 70% perchloric acid (Caledon), prepurified argon (Praxair) and sodium perchlorate (Fisher Scientific) were used as received.

Azidopentaamminecobalt(III) chloride, [(NH<sub>3</sub>)<sub>5</sub>CoN<sub>3</sub>]Cl<sub>2</sub>,<sup>13</sup> bromopentaamminecobalt(III) bromide, [(NH<sub>3</sub>)<sub>5</sub>CoBr]Br<sub>2</sub>,<sup>14</sup> and bromopentaamminecobalt(III) perchlorate, [(NH<sub>3</sub>)<sub>5</sub>CoBr](ClO<sub>4</sub>)<sub>2</sub>,<sup>15</sup> were prepared by standard methods.

Azidopentaamminecobalt(III) nitrate, [(NH<sub>3</sub>)<sub>5</sub>CoN<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, was prepared either by treatment of a solution of the chloride salt with a stoichiometric amount of aqueous AgNO<sub>3</sub> and removing AgCl by filtration through a 0.22 μm Millipore filter or by the following adaptation of the literature synthesis<sup>13</sup> of the chloride salt. To a solution containing 29.9 g of NH<sub>4</sub>NO<sub>3</sub>, 10 g of NaN<sub>3</sub>, 60 mL of water, and 40 mL of concentrated aqueous ammonia was added a solution of 12.2 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 25 mL of water. Air was drawn through the solution for ~2 h, and then the yellow-brown solution was heated on a steam bath for ~2 h until it turned deep purple. The solution was cooled in ice, and the product collected by filtration and washed with cold water, ethanol, and ether. The product was dissolved in 1.0 L of water at 45–50 °C and filtered through a 0.2 μm filter. Then 10 g of NH<sub>4</sub>NO<sub>3</sub> was dissolved in the warm filtrate and, after cooling in ice, the product was collected and washed as before. Yield: 6.7 g.

For the chromophores used here, the observation wavelengths (nm) and molar extinction coefficients (M<sup>-1</sup> cm<sup>-1</sup>) are the following: (NH<sub>3</sub>)<sub>5</sub>-CoN<sub>3</sub><sup>2+</sup>, 516 (268), 350 (1.24 × 10<sup>3</sup>); (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup>, 546 (54.2), 252 (1.74 × 10<sup>4</sup>). These are in good agreement with the values tabulated by Parker and Espenson.<sup>12</sup>

Stock solutions of perchloric acid were made by dilution of 70% HClO<sub>4</sub> and standardized by titration with aqueous NaOH. Stock solutions of sodium perchlorate were prepared from solid NaClO<sub>4</sub> and standardized by titration of the H<sup>+</sup> eluted by an aliquot from a cation exchange column in the H<sup>+</sup> form. Solutions of acetonitrile were made by pipetting appropriate volumes of neat acetonitrile and diluting to the mark with water in a volumetric flask.

Solutions of CuNO<sub>3</sub> in aqueous acetonitrile were prepared by the reaction of AgNO<sub>3</sub> with Cu metal under an argon atmosphere. The reactant solution was prepared to contain the desired amount of acetonitrile (0.095–1.89 M) and HClO<sub>4</sub>, and the Ag metal and excess Cu metal were removed by filtration. A sample of the solution was air oxidized and analyzed for total copper by iodimetry.

Solutions of the cobalt(III) complexes were prepared by diluting a known weight of the required solid to volume in a volumetric flask with water and the desired volumes of stock solutions of HClO<sub>4</sub> and NaClO<sub>4</sub>. The cobalt(III) solutions were stored in the dark to minimize photolytic decomposition. Solutions of (NH<sub>3</sub>)<sub>5</sub>CoN<sub>3</sub><sup>2+</sup> showed no detectable change in absorbance in 4 days, but solutions of (NH<sub>3</sub>)<sub>5</sub>-CoBr<sup>2+</sup> needed to be prepared daily.

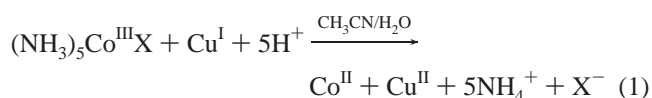
For reactions in the absence of acetonitrile, solutions of Cu(ClO<sub>4</sub>) were prepared by reduction of solutions of Cu(ClO<sub>4</sub>)<sub>2</sub> with Cr(ClO<sub>4</sub>)<sub>2</sub> as described by Parker and Espenson.<sup>12</sup> The aqueous Cr(ClO<sub>4</sub>)<sub>2</sub> was prepared by reduction of Cr(ClO<sub>4</sub>)<sub>3</sub> in aqueous HClO<sub>4</sub> over amalgamated zinc. Most of these solutions were ~3.0 mM in Cu(I), but solutions up to 8 mM were usefully stable with respect to disproportionation. The reduction of (NH<sub>3</sub>)<sub>5</sub>CoN<sub>3</sub><sup>2+</sup> was followed at 350 nm with 2.26 × 10<sup>-4</sup> M Co(III), and the Cu(I) concentration ((1.27–1.45) × 10<sup>-4</sup> M) was determined for each run from the absorbance change of the cobalt(III) complex.

The ionic medium for all the kinetic studies consisted of 0.033 M HClO<sub>4</sub> and 0.11 M NaClO<sub>4</sub>. All the kinetic runs were done under an argon atmosphere and at ambient temperature of 21 ± 1 °C in a

temperature-controlled room. The reactions in the presence of acetonitrile were monitored on a Cary 219 spectrophotometer in 5.00 cm path length cylindrical cells; these reactions were monitored at the absorbance maxima of 516 and 546 nm for (NH<sub>3</sub>)<sub>5</sub>CoN<sub>3</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>-CoBr<sup>2+</sup>, respectively. Those with no acetonitrile were studied on a Tritech Dynamic Instruments stopped-flow system with a 1.0 cm path length cell, described previously.

## Results

**Kinetic Analysis.** The method developed here is based on the measurement of the rate constant for reaction 1 (X = N<sub>3</sub><sup>-</sup> or Br<sup>-</sup>) as a function of the concentration of acetonitrile. The experimental conditions are often such that the initial concentration of the cobalt(III) complex is typically 1.5–4 times larger than the total initial concentration of copper(I), and generally the conditions are second-order, with neither reagent in large excess. The former conditions were selected in order to use the absorbance change to determine the copper(I) concentration, and the general conditions were dictated by the accessible copper(I) concentration and the advantage of having the cobalt(III) chromophore at a concentration that gave an initial absorbance in the range of 0.4–0.8 units.



If  $A_0$  and  $B_0$  represent the initial concentrations of (NH<sub>3</sub>)<sub>5</sub>-Co<sup>III</sup>X and Cu<sup>I</sup>, respectively, and  $A_\infty$  is the final concentration of A, then the reaction stoichiometry gives  $B_0 = A_0 - A_\infty$ . The initial absorbance is  $I_0 = l\epsilon_A A_0$ , and the final absorbance is  $I_\infty = l\epsilon_A A_\infty$ , where  $\epsilon_A$  is the extinction coefficient for A,  $l$  is the cell path length in centimeters, and it is assumed that A is the only absorbing species. Combination of these relationships gives  $B_0$  as

$$B_0 = \frac{I_0 - I_\infty}{l\epsilon_A} \quad (2)$$

In the present experiments, eq 2 can be used to calculate the initial concentration of copper(I) once  $I_0$  and  $I_\infty$  have been determined from the kinetic run.

The absorbance at any time is given by

$$I = l\epsilon_A A \quad (3)$$

where  $A$  is the concentration of (NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>X at any time. The standard integrated form of the second-order rate law (eq 4) can be expressed in exponential form, and then after substitution for the concentration of  $B$  at any time from the stoichiometry relationship that  $A_0 - A = B_0 - B$  and rearrangement, one obtains the time dependence for  $A$  given by eq 5.

$$k_2 t = \frac{1}{B_0 - A_0} \ln \left( \frac{A_0 B}{B_0 A} \right) \quad (4)$$

$$A = \frac{(B_0 - A_0)}{\frac{B_0}{A_0} \exp\{(B_0 - A_0)k_2 t\} - 1} \quad (5)$$

Combination of the relationship between  $I_0$  and  $A_0$  and eq 2 gives the ratio  $B_0/A_0$  as

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$$\frac{B_0}{A_0} = \frac{I_0 - I_\infty}{I_0} \quad (6)$$

The same relationships may be combined to give

$$B_0 - A_0 = -\frac{I_\infty}{l\epsilon_A} \quad (7)$$

Then substitution of eqs 6 and 7 into eq 5 and substitution of the resultant into eq 3 gives the time dependence of the absorbance as eq 8.

$$I = \frac{I_\infty}{\left(\frac{I_0 - I_\infty}{I_0}\right) \exp\left\{-\frac{I_\infty k_2 t}{\epsilon_A}\right\} - 1} \quad (8)$$

The ramifications of this equation are that, under the specified second-order conditions, it is possible to determine the second-order rate constant, if  $\epsilon_A$  for the chromophore is known, by fitting the variation of  $I$  with time. In the actual analysis of the data, eq 8 was modified by adding a term  $I_b$  for the spectrophotometer blank absorbance, and a deadtime  $t_d$  was added to  $t$  to account for the time between mixing and the start of the absorbance measurements. The values of  $I_b$  ( $\sim 0.02$ ) and  $t_d$  ( $\sim 15$  s) are primarily determined from the expected absorbance at zero time that is based on the known values of  $[\text{Co(III)}]$  and  $\epsilon_A$ .

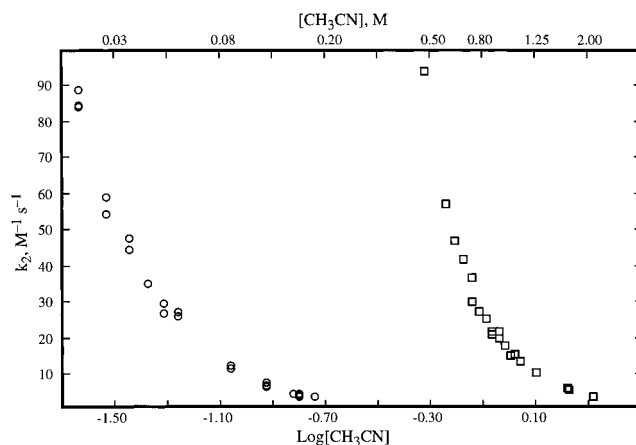
To check the order of the reaction, a number of runs also were done under conditions of  $[\text{Cu(I)}] > [\text{Co(III)}]$ . In these cases, the concentration of Cu(I) in the stock solution was determined from a few runs under the opposite conditions (as described above). Then the stock solution concentration was the basis for the  $[\text{Cu(I)}]$  when  $[\text{Cu(I)}] > [\text{Co(III)}]$ . Then  $B_0$  ( $[\text{Cu(I)}]$ ) and  $A_0$  ( $[\text{Co(III)}]$ ) in eq 5 are known, and this expression for  $A$  was substituted into eq 3 to fit the time dependence of the absorbance.

**Variation of Rate with  $\text{CH}_3\text{CN}$  Concentration.** The kinetic results for reactions with  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  and  $(\text{NH}_3)_5\text{CoBr}^{2+}$  are given in Tables S1 and S2, respectively, of the Supporting Information. The second-order rate constant ( $k_2$ ) was found to be independent of both total copper(I) and total cobalt(III) over the range of acetonitrile concentrations studied, showing that the reaction is first-order in both of these reagents. This is consistent with the earlier observations of Parker and Espenson<sup>12</sup> in aqueous acid. The values of  $k_2$  decrease smoothly as the acetonitrile concentration is increased from 0.024 to 0.18 M with  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  and from 0.57 to 2.0 M with  $(\text{NH}_3)_5\text{CoBr}^{2+}$ . These variations are illustrated in Figure 1. The oxidant was changed to the more reactive  $(\text{NH}_3)_5\text{CoBr}^{2+}$  for the higher acetonitrile range because, otherwise, the reaction became so slow that the kinetics become less reproducible, probably because of dioxygen leakage into the solution.

To explain the variation of  $k_2$  with the acetonitrile concentration, it is assumed that copper(I) is undergoing complexation by acetonitrile (AN) that can be described by overall formation constants ( $\beta_n$ ) defined by

$$\beta_n = \frac{[\text{Cu(AN)}_n^+]}{[\text{Cu}^+][\text{AN}]^n} \quad (9)$$

If these are assumed to be rapidly maintained equilibria, then the concentration of each acetonitrile complex can be expressed



**Figure 1.** Dependence of  $k_2$  on acetonitrile concentration for the reduction of  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  (O) and  $(\text{NH}_3)_5\text{CoBr}^{2+}$  (□) by copper(I) in 0.033 M  $\text{HClO}_4$ /0.11 M  $\text{NaClO}_4$ .

in terms of the total copper(I) concentration,  $[\text{Cu}^+]_{\text{tot}}$ , and the  $\beta_n$  values by the general expression given in

$$[\text{Cu(AN)}_n^+] = \frac{\beta_n [\text{AN}]^n}{1 + \sum_{n=1}^{n=4} \beta_n [\text{AN}]^n} [\text{Cu}^+]_{\text{tot}} \quad (10)$$

If aqueous copper(I) ( $n = 0$ ) and its acetonitrile complexes are assumed to be potential reductants for the cobalt(III) complexes, then the rate of disappearance of cobalt(III) is given by

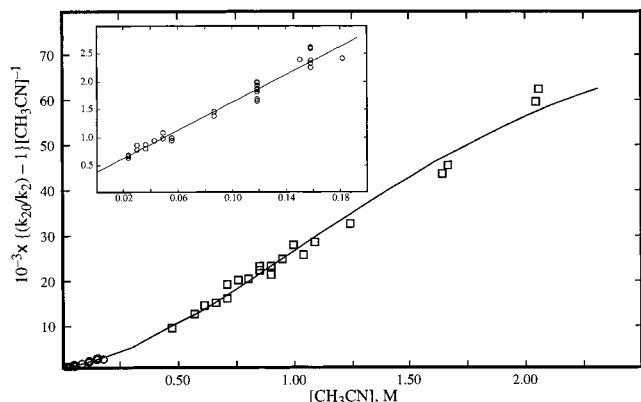
$$\frac{-d[\text{Co}^{\text{III}}]}{dt} = \frac{k_{20} + \sum_{n=1}^{n=4} k_{2n} \beta_n [\text{AN}]^n}{1 + \sum_{n=1}^{n=4} \beta_n [\text{AN}]^n} [\text{Cu}^+]_{\text{tot}} [\text{Co}^{\text{III}}] \quad (11)$$

where  $k_{20}$  is the rate constant for aqueous copper(I) and  $k_{2n}$  is the analogous value for each of the acetonitrile complexes. Therefore the experimental second-order rate constant is predicted to be given by

$$k_2 = \frac{k_{20} + \sum_{n=1}^{n=4} k_{2n} \beta_n [\text{AN}]^n}{1 + \sum_{n=1}^{n=4} \beta_n [\text{AN}]^n} \quad (12)$$

This expression is the direct analogue of that used in spectrophotometric determinations of formation constants in which the molar extinction coefficients would replace the  $k_{2n}$  values. By extension of this analogy, it is well-known that such methods will only be successful if the  $k_{2n}$  values are quite different from  $k_{20}$ . Qualitatively, the fact that the rate decreases as the acetonitrile concentration increases indicates that the  $k_{2n}$  values are smaller than  $k_{20}$ .

Clearly it would be advantageous to reduce the number of parameters needed to describe the system by independently determining the value of  $k_{20}$ . Parker and Espenson<sup>12</sup> have published values of  $k_{20}$  for  $(\text{NH}_3)_5\text{CoBr}^{2+}$  and  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  and Sisley and Jordan<sup>16</sup> also studied the latter complex, but these values are at somewhat different ionic strength than the present



**Figure 2.** Variation  $(k_{20}/k_2 - 1)[\text{CH}_3\text{CN}]^{-1}$  versus  $[\text{CH}_3\text{CN}]$  for the reduction of  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  (○) and  $(\text{NH}_3)_5\text{CoBr}^{2+}$  (□) by copper(I) in 0.033 M  $\text{HClO}_4$ /0.11 M  $\text{NaClO}_4$ .

conditions. Therefore the kinetics of the reaction of aqueous copper(I) with these complexes has been measured by stopped-flow spectrophotometry in 0.033 M  $\text{HClO}_4$  and 0.11 M  $\text{NaClO}_4$ . The reaction of  $2.26 \times 10^{-4}$  M  $(\text{NH}_3)_5\text{CoN}_3^{2+}$  with  $1.36 \times 10^{-4}$  M Cu(I) was monitored at 350 nm and analyzed by the method described above and gave a rate constant of  $(1.42 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , as the average of 15 determinations. This is consistent with the earlier values of  $1.50 \times 10^3$  ( $\mu = 0.20 \text{ M}$ )<sup>12</sup> and  $2.60 \times 10^3$  ( $\mu = 1.0 \text{ M}$ ).<sup>16</sup> With the same stock solution of Cu(I), the reduction of  $3.78 \times 10^{-5}$  M  $(\text{NH}_3)_5\text{CoBr}^{2+}$  was monitored at 252 nm and analyzed by the appropriate second-order equation to obtain a rate constant of  $(4.03 \pm 0.16) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , as the average of 15 determinations. This is consistent with that of  $4.46 \times 10^5$  ( $\mu = 0.20$ )<sup>12</sup> determined earlier. The values of  $k_{20}$  at  $\mu = 0.14 \text{ M}$  were used in eq 13 to analyze the results in the presence of acetonitrile.

For the preliminary analysis, it was assumed that only  $k_{20}$  is contributing to the reduction rate; i.e.,  $\text{Cu}(\text{OH}_2)_m^+$  is a much more reactive reducing agent than any  $\text{Cu}(\text{NCCH}_3)_n^+$  species. Then eq 12 can be rearranged to

$$\left(\frac{k_{20}}{k_2} - 1\right)[\text{AN}]^{-1} = \beta_1 + \beta_2[\text{AN}] + \beta_3[\text{AN}]^2 + \beta_4[\text{AN}]^3 \quad (13)$$

Since  $k_{20}$  is known and  $k_2$  has been measured as a function of  $[\text{AN}]$ , it is possible to plot the LHS of eq 13 versus  $[\text{AN}]$  to provide an initial graphical assessment of the results. Such plots are given in Figure 2, where it is shown that the plot is linear for  $[\text{AN}] \leq 0.18 \text{ M}$ , and the intercept and slope give initial estimates for  $\beta_1$  and  $\beta_2$ , respectively. As the  $[\text{AN}]$  is increased to  $\sim 1 \text{ M}$ , the plot shows the upward curvature that is expected if the higher order terms in  $[\text{AN}]$  in eq 13 are contributing.

As the  $[\text{AN}]$  is increased from  $\sim 1$  to 2.2 M, the curve actually flattens off, rather than continuing the upward curvature expected from the polynomial in eq 13. Clearly this cannot be ascribed to formation of higher complexes and must be due to the breakdown of the assumption that  $\text{Cu}(\text{OH}_2)_m^+$  is the only reactive reductant. This is not unexpected because, as shown later from species distribution curves, the concentration of  $\text{Cu}(\text{OH}_2)_m^+$  falls to inconsequential levels at the higher  $[\text{AN}]$  values.

Further analysis relies on least-squares fitting of the data to eq 12 with the inclusion of various  $k_{2n}$  terms to determine which one(s) may be statistically significant and improve the overall fitting of the data. The problem is primarily with the data for  $[\text{AN}] > 1.0 \text{ M}$  for which the oxidant is  $(\text{NH}_3)_5\text{CoBr}^{2+}$ .

**Table 1.** Summary of Formation Constants from Fitting to Different Models

$(\text{NH}_3)_5\text{CoN}_3^{2+}$		$(\text{NH}_3)_5\text{CoBr}^{2+}$		$\log \beta_n$		
$k_{21}$	$k_{22}$	$k_{22}$	$k_{23}$	$n = 1$	$n = 2$	$n = 3$
$2.9 \pm 2$			$1.92 \pm 0.2$	2.664	3.973	4.295
	$0.5 \pm 0.25$	$7.4 \pm 3$		2.827	4.053	4.305
	$0.5 \pm 0.3$	$9.3 \pm 2.5$	$1.84 \pm 0.2$	2.605	4.001	4.236
				2.640	4.007	4.346

<sup>a</sup> Error limits are one standard deviation.

**Table 2.** Summary of Formation Constants for the Aqueous Copper(I)–Acetonitrile System

$\mu, \text{M}$	$[\text{CH}_3\text{CN}]$ range	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	ref
0.14	0.02–2.0	2.63	4.02	4.30	a
0.50	0.14–1.1		4.35 <sup>g</sup>	$\sim 4.65$	b
0.20	0.01–0.15	3.28	4.35 <sup>g</sup>	4.39 <sup>g</sup>	c
0.20	0.19–1.22		4.35 <sup>g</sup>	4.39	d
0.01	0.001–1.0		3.89	4.11	e
	0.10–2.0		4.35		f

<sup>a</sup> This work. <sup>b</sup> Mi, L.; Zuberbühler, A. *Helv. Chim. Acta* **1991**, *74*, 1679. <sup>c</sup> Gunter, A.; Zuberbühler, A. *Chimia* **1970**, *24*, 340. <sup>d</sup> Zuberbühler, A. *Helv. Chim. Acta* **1970**, *53*, 473. <sup>e</sup> Manahan, S. E.; Iwamoto, T. R. *J. Electroanal. Chem.* **1967**, *14*, 213. <sup>f</sup> Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488. <sup>g</sup> Value assumed from earlier study.

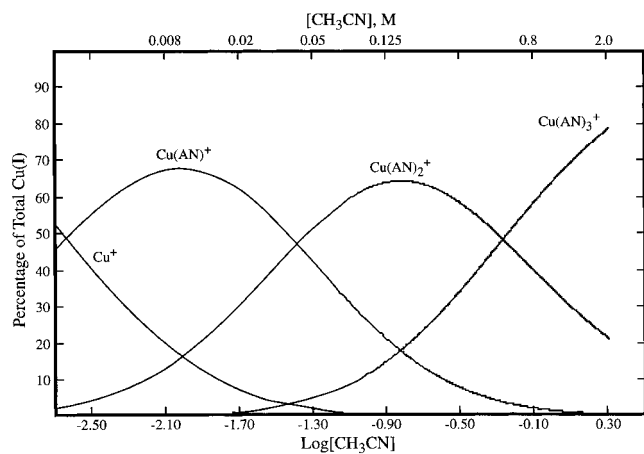
Preliminary species distribution curves reveal that  $\text{Cu}(\text{AN})_2^+$  and  $\text{Cu}(\text{AN})_3^+$  are the dominant species under these conditions. The results of the trial fits with several combinations of  $k_{2n}$  values are summarized in Table 1. The general observation is that any model that includes  $k_{2n}$  values as parameters improves the overall standard error of the fit by about a factor of 2, but no particular model is significantly better than the others, and the values of  $\beta_n$  are rather insensitive to the model. On the basis of the standard errors, the value of  $k_{23}$  for  $(\text{NH}_3)_5\text{CoBr}^{2+}$  is reasonably well defined, but for the other  $k_{2n}$  values, the standard error is only 2–3 times smaller than the value.

In summary, the average  $\beta_n$  values from Table 1 are  $4.3 \times 10^2$ ,  $1.05 \times 10^4$ , and  $1.97 \times 10^4$  for  $n = 1, 2$ , and 3, respectively. These lead to stepwise formation constants ( $K_n$ ) of  $4.3 \times 10^2$ , 24, and 1.9, respectively.

## Discussion

The results of this and previous studies of the aqueous copper(I)–acetonitrile system are summarized in Table 2. A species distribution diagram based on the present results is shown in Figure 3.

In the earliest study<sup>8</sup> using polarography, it was claimed that the potential did not change significantly between 0.1 and 2.0 M  $\text{CH}_3\text{CN}$  and  $\beta_2$  was calculated on the basis of the assumption that the dominant species was the bis complex. The more recent results of Cox et al.<sup>11</sup> indicate that the potential actually does change significantly over the 0.1–2.0 M range, and the present results indicate that both bis and tris complexes would be present, as shown in Figure 3. Therefore, it is not surprising that this earliest value of  $\beta_2$  is somewhat too large. The later polarographic study of Manahan and Iwamoto<sup>9</sup> yielded values of  $\beta_2$  and  $\beta_3$  that are in reasonable agreement with those of the present study, and the differences might be ascribed to the different ionic strengths. Their value of  $\beta_3/\beta_2 = K_3 = 1.67 \text{ M}$  is in good agreement with that determined here (1.9 M) and with values of 1.7–2.2 suggested by Mi and Zuberbühler<sup>10c</sup> from their rate law analysis of the Cu(I)– $\text{CH}_3\text{CN}$ – $\text{O}_2$  system. It is odd that no  $\beta_1$  was evaluated by Manahan and Iwamoto, since their study extended to the lowest concentration of  $\text{CH}_3\text{CN}$ .



**Figure 3.** Species distribution curves for the copper(I)–aqueous acetonitrile system in 0.033 M HClO<sub>4</sub>/0.11 M NaClO<sub>4</sub> calculated for total [Cu(I)] = 1.0 × 10<sup>-3</sup> M.

**Table 3.** Formation Constants for Aqueous Copper(I) with Some Common Ligands

ligand	log K <sub>n</sub> (log β <sub>n</sub> ) <sup>a</sup>			
	n = 1	n = 2	n = 3	n = 4
CH <sub>3</sub> CN <sup>b</sup>	2.63	1.39 (4.02)	0.27 (4.29)	
NH <sub>3</sub>	5.93	4.65 (10.58)		
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	6.83	4.10 (10.73)		
C <sub>5</sub> H <sub>5</sub> N	4.84	2.75 (7.59)	0.59 (8.18)	0.34 (8.52)
(NH <sub>2</sub> ) <sub>2</sub> CS	7.7 <sup>c</sup>	4.6 <sup>d</sup> (12.3)	2.0 (14.3)	1.2 (15.5)
Cl <sup>-</sup>	3.10	2.32 (5.42)	-0.67 (4.8)	
Br <sup>-</sup>	3.53	2.33 (5.86)	0.57 (6.43)	
I <sup>-</sup>	5.7	3.0 (8.7)	1.7 (10.43)	
CN <sup>-</sup>	14.4 <sup>c</sup>	7.3 <sup>d</sup> (21.7)	5.7	1.1

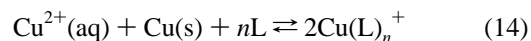
<sup>a</sup> Unless otherwise indicated, from: Smith, R. M.; Martell, A. E.; Motekaitis, R. *NIST Critically Selected Stability Constants of Metal Complexes Database*, Version 2; NIST: Washington, DC, 1995. <sup>b</sup> This work. <sup>c</sup> Estimated from E<sub>B</sub>, C<sub>B</sub>, and D<sub>B</sub> parameters in ref 20. <sup>d</sup> Calculated from the measured β<sub>2</sub> and the estimated β<sub>1</sub>.

Of all the values in Table 2, the major discrepancy involves the β<sub>1</sub> determined here and that of Gunter and Zuberbühler.<sup>10a</sup> Their value was determined by a kinetic method with O<sub>2</sub> as the scavenger for Cu(I), and their analysis assumed the earlier value of β<sub>2</sub> determined by Hemmerich and Sigwart.<sup>8</sup> As noted above, this β<sub>2</sub> is probably too large, but a consideration of eq 12 or 13 would suggest that this would have the effect of giving too small a value for β<sub>1</sub>. It is apparent from the intercept (β<sub>1</sub>) of the insert in Figure 1 that the present results are not consistent with the β<sub>1</sub> = 1.9 × 10<sup>3</sup> M determined by Gunter and Zuberbühler. A possible explanation is suggested by the results of Sharma and Millero<sup>17</sup> on the Cu(I)–Cl<sup>-</sup> system, where it is proposed that both aqueous Cu(I) and CuCl are reactive reductants for O<sub>2</sub>. The analysis of Gunter and Zuberbühler assumed that aqueous Cu(I) was the only reductant. It should be noted that Sharma and Millero found k<sub>20</sub> = 4.8 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> for aqueous Cu<sup>+</sup> + O<sub>2</sub> at pH 8.0, while Zuberbühler used (3.5–4.1) × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> at pH 2–5.<sup>10a,b</sup> This difference may be due to an [H<sup>+</sup>]<sup>-1</sup> dependent term in the rate law that was tentatively identified by Mi and Zuberbühler.<sup>10c</sup>

The formation constants of aqueous copper(I) with some common monodentate ligands are summarized in Table 3. The values for acetonitrile are generally the smallest but are nonetheless surprising because acetonitrile is often considered

to be a very weakly complexing ligand. The latter perception is based on experience and is consistent with common measures of ligand basicity such as Gutmann donor numbers<sup>18</sup> or the E and C parameters of Drago.<sup>19</sup> Recently Hancock and Martell<sup>20</sup> have proposed an analogue of the latter scale for complexation in aqueous solution in which each acid and base is characterized by E, C, and D parameters. The β<sub>1</sub> values for acetonitrile with Ag<sup>+</sup><sup>21</sup> and Cu<sup>+</sup> can be used along with the available acid parameters<sup>20</sup> to estimate for acetonitrile that E<sub>B</sub> ≈ 0 and C<sub>B</sub> ≈ 6, if the steric factor D<sub>B</sub> = 0.

From the standpoint of aqueous copper(I) chemistry, it is noteworthy that the problem of disproportionation can be overcome by complexation of copper(I). This may be evaluated in terms of the reaction



In the absence of L, the equilibrium constant for this reaction in water is K<sub>C</sub> = 7.7 × 10<sup>-7</sup> M, and the equilibrium constant for eq 14 is given by K<sub>14</sub> = K<sub>C</sub>(β<sub>n</sub>)<sup>2</sup>. Clearly if β<sub>n</sub> ≥ 10<sup>3.5</sup>, this equilibrium will favor the copper(I) species. In practical terms, this means that a solution initially containing ≤ 5 mM Cu<sup>2+</sup> and 0.2 M CH<sub>3</sub>CN (~1.2 mL in 100 mL) in contact with excess copper metal will react to give >97% of the dissolved copper as Cu<sup>+</sup> at twice the original concentration of Cu<sup>2+</sup>. Other ligands in Table 3 with larger β<sub>n</sub> values will produce the same result at lower ligand concentrations, but acetonitrile is the chemically most innocuous and therefore advantageous for further applications of such solutions to copper(I) chemistry.

The kinetic method for determining formation constants with copper(I) in aqueous solution has the obvious advantages of using convenient reagents and instrumentation. The absorbance change of the cobalt(III) complex can be used both to determine the rate constant and to determine the total copper(I) in the solution. This does require a second-order kinetic analysis but is not a major disadvantage because the concentration and extinction coefficient of the cobalt(III) chromophore are easy to determine accurately and evidence here and elsewhere<sup>12</sup> indicates that these are cleanly second-order reactions. The method is adaptable to various magnitudes of β<sub>n</sub> values by choosing the appropriate cobalt(III) complex, as illustrated here with (NH<sub>3</sub>)<sub>5</sub>CoN<sub>3</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup>. For smaller β<sub>n</sub> values one could use a complex with a smaller k<sub>20</sub>, such as (NH<sub>3</sub>)<sub>5</sub>-CoF<sup>2+</sup> (k<sub>20</sub> = 1.1)<sup>12</sup> or (NH<sub>3</sub>)<sub>5</sub>CoCN<sup>2+</sup> (k<sub>20</sub> = 3.3 × 10<sup>-3</sup>).<sup>12</sup> The method is obviously limited to polar solvents that dissolve the cobalt(III) complexes and minimize ion-association complications. The latter also could be more of a problem with anionic ligands and the more highly charged cobalt(III) complexes and might constrain the upper limit of the ligand concentration.

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**Supporting Information Available:** Reagent concentrations and observed and calculated rate constants for the reduction of (NH<sub>3</sub>)<sub>5</sub>-CoN<sub>3</sub><sup>2+</sup> (Table S1) and (NH<sub>3</sub>)<sub>5</sub>CoBr<sup>2+</sup> (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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