

Nature of the 2-, 3-, 4-Cyanopyridine, 3-Aminocrotonitrile, and 3-Aminobutyronitrile Complexes of Copper(I) in Propylene Carbonate

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The stoichiometry, stability, and mode of coordination of the 2-, 3-, 4-cyanopyridine, 3-aminocrotonitrile, and 3-aminobutyronitrile complexes of copper(I) in propylene carbonate were investigated by polarography, potentiometry, and infrared spectroscopy. No evidence for the formation of the 1:1 complexes was observed. 2-Cyanopyridine, 3-cyanopyridine, and 3-aminobutyronitrile form 2:1 complexes, while 4-cyanopyridine and 3-aminocrotonitrile form 2:1 and 3:1 complexes over the range of copper(I) and ligand concentrations examined. The cyanopyridines are coordinated to copper(I) ion through the pyridine nitrogen, and the two aminonitriles are coordinated through the amine nitrogen.

Introduction

In a previous study in this laboratory on the influence of the solvent on the orientation of 3-butene nitrile and 3-dimethylaminopropionitrile in the coordination sphere of copper(I) and silver(I) ions,² it was shown that in a nonpolar medium coordination of the polar nitrile group to the metal ions is favored, while in a polar medium coordination by the nonpolar olefinic and tertiary amine groups is favored. These results and those on the solid complexes of 2-, 3-, and 4-cyanopyridine and copper(I) perchlorate³ suggested an examination of the copper(I) complexes of 2-, 3-, 4-cyanopyridine, 3-aminocrotonitrile, and 3-aminobutyronitrile in solution. Propylene carbonate, donor number 15(DN_{SbCl₅} = 15),⁴ and possessing good characteristics for electrochemical studies,^{5,6} was, interestingly, the only one of a number of weakly solvating polar solvents examined in which the cyanopyridine complexes of copper(I) perchlorate were soluble. We report in this paper, the nature (mode of coordination, stoichiometry, and stability) of the copper(I) complexes of 2-, 3-, and 4-cyanopyridine, 3-aminocrotonitrile, and 3-aminobutyronitrile in propylene carbonate.

(1) On leave from the University of Zagreb, Yugoslavia.

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Experimental Section

Propylene carbonate (J. T. Baker, practical grade, and Aldrich Chemical Co.) was purified by passage through a 18-cm (i.d.) \times 45-cm column packed with Woelm, activity grade 1, neutral alumina, followed by fractional distillation at ca. 1 mm pressure. Of ca. 1300 ml of propylene carbonate, the first 150-200 ml of the distillate was discarded and the fraction distilling at 65-67°, ca. 800 ml, was collected. The major polarographic impurity in the original propylene carbonate was a substance which gave an anodic wave starting at ca. +0.2v vs. S.C.E. (aqueous). One tenth formal tetraethylammonium perchlorate solutions of the purified propylene carbonate gave with the dropping mercury electrode (DME) current-voltage curves with low background current and a potential range of +0.6 to -2.3v vs. S.C.E. (aqueous). Water in the purified propylene carbonate was determined by gas chromatography.⁷ An F & M chromatograph, Model 700, equipped with a thermal conductivity detector was used with a 2-ft column of Porapak Q (80-100 mesh). Values of 150-200 ppm were obtained for the water content. The solvent was kept under nitrogen, and all solution preparations, as well as other sample manipulations, were carried out in a dry nitrogen atmosphere. Dry nitrogen obtained from Union Carbide Corp., Linde Division, was passed first through a copper furnace, then through a column of 4A Linde Molecular Sieves.

Reagent grade hexaaquocopper(II) perchlorate (G. F. Smith, Chemical Co.) was dried in a vacuum oven at 85° and stored over anhydrous magnesium perchlorate. From the analysis of the salt, the formula Cu(ClO₄)₂·4H₂O was obtained. The cyanopyridines were obtained from Aldrich Chemical Co. and were used without further purification. 3-Aminocrotonitrile (Aldrich Chemical Co.) was purified by vacuum sublimation, and 3-aminobutyronitrile (Chemical Procurement Lab.) was used without further purification. Analytical grade copper wire was cleaned with dilute nitric acid, washed with distilled water, and dried with acetone. Tetraethylammonium perchlorate (Eastman Organic) was recrystallized twice from water and dried at 100°.

Copper amalgams for potentiometric and polarogra-

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two parts, as shown in Figure 1. The first cathodic peak measurements were prepared by electrolysis of dilute aqueous perchloric acid solutions containing measured amounts of copper(II) nitrate, using weighed amounts of mercury as the cathode. The procedure and the electrolysis cell for this preparation have been described previously.⁸ Amalgams for potentiometric measurements were 0.2M in copper and for polarographic measurements with the dropping amalgam electrode (D.A.E.) $5 \times 10^{-4}M$. Potentiometric measurements were made with a Leeds and Northrup K-3 potentiometer at $25.0 \pm 0.1^\circ$.

Stock solutions of copper(I) perchlorate were prepared by the treatment of solutions of copper(II) perchlorate ($2.5 \times 10^{-4}F$) in propylene carbonate with copper wire at 90° for three hr. Purified nitrogen presaturated with propylene carbonate at 90° was passed through the solutions continuously. Appropriate aliquots of these solutions were diluted to prepare the solutions for measurement.

The current-voltage curves were recorded using a controlled potential polarograph of the type designed by Kelley, Fisher, and Jones.^{9,10} Modifications of the original design have been described.¹¹ A polarographic cell previously described¹² was modified by adding a third compartment, connected through a medium porosity sintered glass frit, to the working electrode compartment. All polarographic and potentiometric measurements were carried out in 0.1 F tetraethylammonium perchlorate solution of propylene carbonate.¹³ The Hg | Hg₂Cl₂, KCl(sat'd), (C₂H₅)₄NClO₄ (0.10F) electrode in propylene carbonate was used as the reference electrode.¹⁴

Infrared spectral data were obtained with a Perkin-Elmer Model 421 spectrophotometer. Barium fluoride cells were used in the examinations.

Results and Discussion

Stoichiometry and Stability of the Copper(I) Complexes Polarographic Studies. Propylene carbonate solutions of copper(I) perchlorate 0.10 F in tetraethylammonium perchlorate have been reported to yield composite anodic-cathodic polarographic curves which pass through zero current without inflection and with 0.059/n values of 60 and 55 millivolts for the anodic and cathodic sections, respectively.¹⁵ Half-wave potentials of +0.610v (copper(II), copper(I)) and +0.525v (copper(I), copper(Hg)) vs. S.C.E. (aqueous) were reported. The polarography of solutions of propylene carbonate containing copper(II) perchlorate has also been described by Gutmann *et al.*⁶

In this study, we have analyzed the composite anodic-cathodic polarographic curves of copper(I) perchlorate solutions 0.10 F in tetraethylammonium perchlorate and obtained the following values for $E_{1/2}$ -Cu(II), Cu(I) and $E_{1/2}$ -Cu(I), Cu(Hg) vs. the Hg | Hg₂Cl₂, KCl(sat'd), (C₂H₅)₄NClO₄(0.10F) electrode in propylene carbonate: +0.570 and +0.520v.

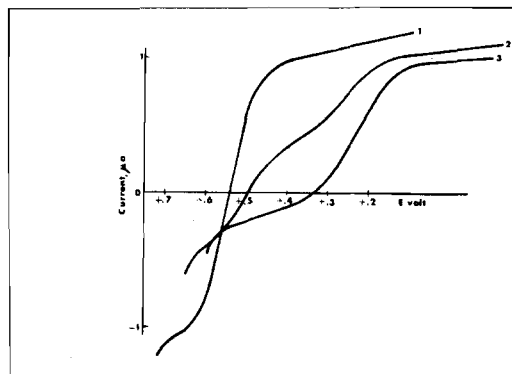


Figure 1. Effect of 3-aminocrotononitrile on the polarographic wave for propylene carbonate solutions of copper(I) perchlorate, 0.10 F tetraethylammonium perchlorate. Curve 1. The composite anodic-cathodic wave for $5 \times 10^{-4}F$ copper(I) perchlorate solution. Curve 2. The copper(I), copper(Hg) step for $5 \times 10^{-4}F$ copper(I) perchlorate solution $6.0 \times 10^{-4}F$ in 3-aminocrotononitrile. Curve 3. The copper(I), copper(Hg) step for $5 \times 10^{-4}F$ copper(I) perchlorate solution $1.2 \times 10^{-3}F$ in 3-aminocrotononitrile.

With an excess of the ligands, the cathodic portion of the composite anodic-cathodic polarographic curves of copper(I) perchlorate solutions shifts to more negative potentials. The reduction step remains reversible with 0.059/n values of 58-62 mv. In the cases of 4-cyanopyridine, 3-aminocrotononitrile, and 3-aminobutyronitrile when the total concentration of ligand is less than two times the concentration of copper(I), the cathodic section of the wave is split into

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(13) A typical set of polarographic and potentiometric data is as follows:

Polarography ($5.0 \times 10^{-4}F$ CuClO ₄) [4-cyanopyridine]		Potentiometry ($1.31 \times 10^{-3}F$ CuClO ₄) [3-aminobutyronitrile] $\times 10^3$	
$E_{1/2}$ (mv)*		E (mv)*	
0.00110	+243	0	+456
0.00125	+235	0.197	+450
0.00141	+228	0.478	+439
0.00158	+222	1.05	+404
0.0020	+215	1.36	+374
0.0040	+165	1.61	+302
0.0060	+135	1.89	+212
0.0080	+115	2.17	+171
0.0100	+103	2.45	+82
0.020	+50	2.72	-24
0.040	00	2.98	-58
0.060	-28	3.26	-80
0.080	-55	3.50	-95
0.100	-76	3.80	-106
		4.03	-115
		4.29	-124
		4.55	-130
		4.95	-138
		5.42	-147
		5.92	-155
		7.32	-173
		9.11	-187
		10.8	-198
		15.0	-216
		18.7	-228
		21.8	-234
		24.6	-241

* propylene carbonate calomel reference electrode.

(14) I. Piljac and R. T. Iwamoto, submitted for publication.

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step is the reduction of free copper(I) and the current i_1 , follows the relationship¹⁶

$$i_1 = i_{dc} \left(1 - \frac{y}{2} \right)$$

where i_{dc} is the total cathodic diffusion current and y is the ratio of the total concentration of ligand to the total concentration of copper(I). The second step involves the reduction of the 2:1 complex. With 2-cyanopyridine, the cathodic section was distorted, but not split.

The 2-cyanopyridine-copper(I) complex species in $5 \times 10^{-4} F$ copper(I) perchlorate over the range of 10^{-2} to $10^{-1} F$ ligand is $\text{Cu}(2\text{-cyanopyridine})_2^+$. The slope of the plot of $E_{1/2\text{Cu(I)}, \text{Cu(Hg)}}$ vs. $-\log[2\text{-cyanopyridine}]_T$ was 2.2×0.059 (subscript T denotes total concentration). The overall stability constant β_2 (calculation based on equation below)¹⁷ is $10^{8.7 \pm 0.2}$.

$$(E_u)_c - (E_u)_s = 0.059 \left(\log \frac{1}{\beta_2} - \log \frac{f_s}{f_c} - \log \frac{k_c}{k_s} - 2 \log f_i C_L \right)$$

The ratio k_c/k_s was calculated from the corresponding diffusion current constants, and f_s/f_c and f_L were assumed to be one.

The complex species of 3-cyanopyridine and copper(I) ion in 1×10^{-4} copper(I) perchlorate solution over the range of 5×10^{-3} to $10^{-1} F$ 3-cyanopyridine is the 2:1 complex. The plot of $E_{1/2\text{Cu(I)}, \text{Cu(Hg)}}$ vs. $-\log[3\text{-cyanopyridine}]_T$ is a straight line with a slope of 2.1×0.059 . The overall stability constant β_2 for the complex was found to be $10^{10.6 \pm 0.2}$.

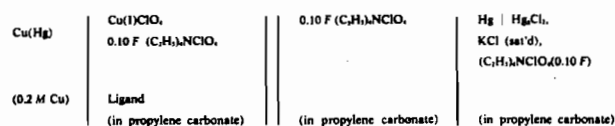
The 3:1 complex $\text{Cu}(4\text{-cyanopyridine})_3^+$ appears to be the principal complex species of 4-cyanopyridine and copper(I) ion in $5 \times 10^{-4} F$ copper(I) perchlorate solutions 10^{-2} to $10^{-1} F$ in 4-cyanopyridine. The slope of the plot of $E_{1/2\text{Cu(I)}, \text{Cu(Hg)}}$ vs. $-\log[4\text{-cyanopyridine}]_T$ in this region of ligand concentration is 3.0×0.059 . (Similar results were obtained using the dropping copper amalgam electrode.) From 3.2×10^{-3} to $1.5 \times 10^{-3} F$ ligand concentration, the plot of $E_{1/2\text{Cu(I)}, \text{Cu(Hg)}}$ vs. $-\log[4\text{-cyanopyridine}]_T$ assumes a slope close to 2×0.059 , indicating the $\text{Cu}(4\text{-cyanopyridine})_2^+$ complex species to be the principal species in this range of ligand concentration. The overall stability constants β_3 and β_2 are $10^{13.0 \pm 0.2}$ and $10^{10.7 \pm 0.7}$, respectively. When the formal 4-cyanopyridine concentration is less than 10^{-3} , the cathodic portion of the polarogram is split into two parts consistent with the formation of a stable 2:1 4-cyanopyridine-copper(I) complex species.

Two complexes, $\text{Cu}(3\text{-aminocrotonitrile})_3^+$ and $\text{Cu}(3\text{-aminocrotonitrile})_2^+$, are formed in $5 \times 10^{-4} F$ copper(I) perchlorate solutions containing 3-aminocrotonitrile up to $10^{-1} F$. Over the concentration range of 10^{-2} to $10^{-1} F$, the 3:1 complex is the principal complex species; the plot of $E_{1/2\text{Cu(I)}, \text{Cu(Hg)}}$ vs. $-\log[3\text{-aminocrotonitrile}]_T$ in this region of ligand concentration is a straight line with a slope of 2.9×0.059 . A value of $10^{13.3 \pm 0.2}$ was obtained for β_3 . Over the

concentration range of 3×10^{-4} to $1 \times 10^{-3} F$ 3-aminocrotonitrile, the cathodic section of the polarograms of $5 \times 10^{-4} F$ copper(I) perchlorate solutions is a split wave. The variation of the ratio of the heights of the two cathodic waves with the concentration of ligand is consistent with the formation of the 2:1 complex $\text{Cu}(3\text{-aminocrotonitrile})_2^+$. A value of $10^{11.0 \pm 0.7}$ was obtained for β_2 from $E_{1/2(\text{complex})}$ values at low ligand concentrations.

The 3-aminobutyronitrile-copper(I) complex species formed in $5 \times 10^{-4} F$ copper(I) perchlorate solutions 10^{-2} to $10^{-1} F$ in 3-aminobutyronitrile is $\text{Cu}(3\text{-aminobutyronitrile})_2^+$. The plot of $E_{1/2\text{Cu(I)}, \text{Cu(Hg)}}$ vs. $-\log[3\text{-aminobutyronitrile}]_T$ over this range of ligand concentration is a straight line with a slope of 2.2×0.059 . The constant β_2 was found to be $10^{15.3 \pm 0.2}$.

Potentiometric Studies. The potential of a copper amalgam electrode immersed in propylene carbonate solutions 9×10^{-5} to $10^{-3} F$ in copper(I) perchlorate and maintained at constant ionic strength ($0.10 F$ tetraethylammonium perchlorate) obeyed the Nernst equation. Above $10^{-3} F$ copper(I) perchlorate, the plot of the potential of the amalgam electrode vs. $\log[\text{Cu(I)}]$ indicates irreversible behavior, probably because of increasing equilibrium ratio of copper(II) to copper(I). Potentiometric studies of the complex-formation systems carried out with $10^{-3} F$ copper(I) solutions (upper limit of concentration of copper(I) solutions in which reversible behavior was observed) gave results in agreement with those obtained by polarography. In the potentiometric study, the concentrations of total copper(I) and of tetraethylammonium perchlorate were kept constant by using solutions of ligand with the same concentrations of copper(I) perchlorate and of tetraethylammonium perchlorate as in the solutions being measured. The potentiometric cell was



In the case of 2-cyanopyridine, the potentiometric titration curve showed a break at ligand to metal ratio of 2:1. Analysis of the potential data beyond the break, with the assumption that all the copper(I) is in the form of the 2:1 complex, gave a linear relationship between the potential of the indicator electrode and the negative logarithm of the free ligand concentration. The slope of 2.1×0.059 indicates $\text{Cu}(2\text{-cyanopyridine})_2^+$ as the highest complex species in the concentration range studied.¹⁸ A value of $10^{9.0 \pm 0.2}$ was calculated for β_2 (polarographic value, $10^{8.7}$). The concentration of copper(I) ion was obtained from the Nernst equation.

The highest 3-cyanopyridine-copper(I) complex indicated by the potentiometric study is the 2:1 species, as in the polarographic study. A straight line with a slope of 2×0.059 was found for the plot of E vs. $-\log[3\text{-cyanopyridine}]$ obtained from the addi-

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tion of 3-cyanopyridine solutions to a saturated solution of $\text{Cu}(\text{3-cyanopyridine})_2\text{ClO}_4$. (The preparation of this perchlorate salt has been described previously³). The overall constant β_2 was calculated to be $10^{10.7 \pm 0.3}$ (polarographic value, $10^{10.6}$).

For the 4-cyanopyridine-copper(I) complex-formation system, the potentiometric data show a large change in potential at ligand to metal ratio of 2:1. Analysis of the potential data beyond the break yielded a plot of potential *versus* the negative logarithm of the free ligand concentration with a slope of 3.0×0.059 , indicating $\text{Cu}(\text{4-cyanopyridine})_3^+$ is the principal complex species present. The value of β_3 , $10^{12.3 \pm 0.1}$, is in fair agreement with the value obtained polarographically ($10^{13.0}$).

The 3:1 complex $\text{Cu}(\text{3-aminocrotonitrile})_3^+$ was indicated by the potential data for the 3-aminocrotonitrile-copper(I) perchlorate solutions to be the highest complex obtainable in the solutions examined. The β_3 value obtained from this study is $10^{13.5 \pm 0.1}$ (polarographic value, $10^{13.3}$).

The potential data for 3-aminobutyronitrile-copper(I) perchlorate solutions beyond the large break at ligand to metal ratio of 2:1 do not indicate formation of a higher complex species than $\text{Cu}(\text{3-aminobutyronitrile})_2^+$. The plot of the potential of the indicator electrode *versus* the negative logarithm of the free ligand concentration has a slope of 2.0×0.059 . For β_2 , a value of $10^{15.1 \pm 0.2}$ was obtained (polarographic value, $10^{15.3}$).

No evidence for polynuclear complex species was obtained from studies of solutions in which the concentration of copper(I) perchlorate was varied by a factor of 10. Much greater variation in copper(I) concentration is not possible because of the low solubility of the complexes and difficulty in preparing more concentrated stock solutions of copper(I) perchlorate.

Mode of Coordination. Infrared Study. The coordination site of copper(I) ion in the complexes with 2-, 3-, 4-cyanopyridine, 3-aminocrotonitrile, and 3-aminobutyronitrile has been determined from the nitrile stretching, C-C and C-N stretching (of the pyridine ring), and the N-H stretching frequencies.

Coordination of the free pair of electrons on the nitrile nitrogen results in a shift of the stretching frequency of the nitrile group to a higher value than that for the free nitrile.¹⁹⁻²⁵ On coordination of the pyridine nitrogen, the four principal bands of pyridine between $1430\text{--}1600\text{ cm}^{-1}$ and the bands for the ring breathing and C-H in-plane deformation frequencies shift to higher values than those for uncoordinated pyridine.^{26,27} When the free electron pair on the amine nitrogen is involved in coordination, the N-H stretching frequencies are shifted to lower values than

those for free amine.²⁸ Although propylene carbonate with a large number of bands in the infrared region is a relatively poor solvent for infrared studies, information on the $\text{C}\equiv\text{N}$, the N-H, and the highest ring stretching frequencies can be obtained.

In the 2-cyanopyridine-copper(I) perchlorate solutions, the nitrile frequency for 2-cyanopyridine at 2240 cm^{-1} remains unchanged. The ring stretching frequency at 1576 cm^{-1} , however, shifts to 1590 cm^{-1} (blue shift), indicating that the pyridine nitrogen is coordinated to copper(I) ion. This information was not expected on the basis of previous results obtained on the solid complex, in which the nitrile nitrogen was found to be coordinated to copper(I) ion.³

Because of the low solubility of the perchlorate salt of the 2:1 3-cyanopyridine-copper(I) complex in propylene carbonate, no infrared study of the mode of coordination of 3-cyanopyridine to copper(I) ion was possible.

The complexes of 4-cyanopyridine and copper(I) ion in propylene carbonate involve pyridine nitrogen coordination. In the spectra of 4-cyanopyridine-copper(I) perchlorate solutions, the ring stretching band at 1590 cm^{-1} is shifted blue to 1610 cm^{-1} , while the nitrile stretching frequency at 2240 cm^{-1} shows no change.

3-Aminocrotonitrile can be obtained in two crystalline forms with melting points of $52\text{--}53$ and $79\text{--}83^\circ$.²⁹ The two forms are the *cis* and *trans* (with respect to the amino and nitrile groups) isomers.³⁰ The isomer used in our study is the *cis* form, according to the study of Conn and Taurins. It had a melting point of 52° and an identical infrared spectrum with that for the isomer obtained by recrystallization from ethanol, which Conn and Taurins concluded to be the *cis* compound. The nitrile stretching frequency of this conjugated nitrile (2195 cm^{-1}) is lower than that for *trans* crotonitrile (2223 cm^{-1})³¹ because of the electron donating amino group on the β carbon.³² On complex-formation of 3-aminocrotonitrile and copper(I) ion, the nitrile frequency shifts from 2195 cm^{-1} to 2220 cm^{-1} - an indication of nitrile coordination. The bands at 3475 and 3380 cm^{-1} in the N-H stretching region, however, also shift (to lower frequency than those for free amino group), indicating coordination by the amine group. This situation can be reconciled by considering the nitrile frequencies of *trans* crotonitrile (2223 cm^{-1}) and 3-aminocrotonitrile (2195 cm^{-1}). The lower frequency of the nitrile stretching vibration in 3-aminocrotonitrile than in crotonitrile, we pointed out earlier, is due to the electron donating amino group on the β carbon. Coordination of the amino group to copper(I) ion decreases the electron donating ability of the amino group and, therefore, the nitrile stretching frequency of coordinated 3-aminocrotonitrile appears at only a slightly lower value than that for crotonitrile.

The infrared data for 3-aminobutyronitrile-copper(I) solutions are consistent with coordination of cop-

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per(I) ion by the amino group. The nitrile frequency at 2240 cm^{-1} for uncoordinated 3-aminobutyronitrile is not affected by coordination of the aminonitrile, and the N-H stretching band at 3370 cm^{-1} is shifted red, down to 3300 cm^{-1} .

In conclusion, in propylene carbonate solution 2- and 4-cyanopyridine are coordinated to copper(I) ion through the pyridine nitrogen and 3-aminocrotonitrile and 3-aminobutyronitrile through the amine nitrogen. Coordination by the pyridine nitrogen in the 2-cyanopyridine complex in propylene carbonate is contrary to that in the solid complex in which nitrile coordination of copper(I) has been found. Because of the similarity of the stability constants for the 2:1 complexes of the three cyanopyridines with copper(I) ion in propylene carbonate and the results of the infrared examination of solid $(3\text{-cyanopyridine})_2\text{ copper(I) perchlorate}$ there is very little doubt that in the $(3\text{-cyanopyridine})_2\text{ copper(I) ion}$ in propylene carbonate the pyridine nitrogens are coordinated to cop-

per(I) ion. The order of stability of the 2:1 complexes of copper(I) is: 2-cyanopyridine < 3-cyanopyridine ~ 4-cyanopyridine < 3-aminocrotonitrile < 3-aminobutyronitrile. The inability to detect the 1:1 complexes indicates that the values of K_{f1} and K_{f2} (the stepwise formation constants) are close together or $K_{f1} < K_{f2}$. This situation is similar to that observed for the copper(I)-ammonia, silver(I)-ammonia, and silver(I)-amine complex-formation systems.³³

The reason for the formation of 3:1 complexes in the cases of 4-cyanopyridine and 3-aminocrotonitrile and not the others is not clearly understood.

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