Tetracoordination of Copper(I) by Monofunctional Amines

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The highest complexes of the monofunctional amines pyridine, quinoline, isoquinoline, piperidine, n- and sec-butylamine, aniline, p-methoxyaniline, and N-benzylidenemethylamine with copper(I) ion in propylene carbonate have been determined by polarography. A maximum coordination of four ligands has been noted in the cases of pyridine and isoquinoline. Solid tetrakis(pyridine)copper(I) perchlorate has been isolated, and by infrared examination of 3:1, 4:1, and 5:1 mole-ratio mixtures of the monofunctional amines with tetrakis(acetonitrile)copper(I) perchlorate, the tetracoordination of quinoline, isoquinoline, piperidine, and N-benzylidenemethylamine to copper(I) has been established. The polarographic data have been used to estimate the appropriate overall stability constants in propylene carbonate.

Introduction

The literature on copper(I) complexes does not appear to contain any definitive information on tetracoordination of copper(I) by monofunctional amines. Recently, we reported on the formation of the 4:1 pyridine-copper(I), nicotinamide-copper(I), and isonicotinamide-copper(I) complex species in propylene carbonate and the isolation of the solid Cu(pyridine)₄-ClO₄.[1] The results of further examination of the maximum number of the monoamines quinoline; isoquinoline; piperidine; n-, sec-, $tert$-butylamine; aniline; p-methoxyaniline; and N-benzylidenemethylamine which enter into coordination with copper(I) ion (*i.e.*, ligand number) are presented in this paper.

Experimental Section

Material. Propylene carbonate, practical grade, was purified by passage through a column (1.8 cm (i.d.)×45 cm) of Woelm, activity grade 1, neutral alumina, followed by fractional distillation at reduced pressure. The purification procedure was repeated until the distillate showed a low polarographic residual current with 0.1 F tetraethylammonium perchlorate as supporting electrolyte.

Tetrakis(acetonitrile)copper(I) perchlorate was prepared as described previously[2] and was recrystallized several times from acetonitrile and dried under nitro-

gen. Tetraethylammonium perchlorate (Eastman Organic Chemicals) was recrystallized two to three times from water and dried at 110°. Current-voltage curves at the dropping mercury electrode of 0.1 F solutions of the purified tetraethylammonium perchlorate in propylene carbonate showed no waves indicative of any electroactive impurities. Hexaaquocopper(II) perchlorate (G. F. Smith Chemical Co.) was dried in a vacuum oven at 75° and stored over anhydrous magnesium perchlorate. On the basis of a copper analysis of the salt by EDTA titration, the composition $Cu(ClO_4)_2 \cdot 3.5H_2O$ was established. Analytical grade copper wire was cleaned with dilute nitric acid, washed with distilled water, and dried with acetone.

Pyridine (Matheson Coleman and Bell, Spectroquality, and J. T. Baker Chemical Co., Baker Analyzed reagent) was used without further purification. Quinoline (Matheson Coleman and Bell Co., practical grade) was dried over potassium hydroxide, then refluxed over sodium metal and distilled at reduced pressure. A colorless liquid was obtained, which changed gradually to yellow on exposure to air. Isoquinoline (Matheson Coleman and Bell, practical grade) was dried over calcium hydride, followed by vacuum distillation. The colorless distillate turned yellow more rapidly than did quinoline. Piperidine (Matheson Coleman and Bell) was purified by drying over potassium carbonate, then refluxing over and distilling from phosphorus(V) oxide.[3] n-Butylamine, sec-butylamine, and $tert$-butylamine (all from Matheson Coleman and Bell) were dried and distilled over potassium hydroxide.[4] Aniline (Matheson Coleman and Bell, reagent grade) was dried over potassium hydroxide for one week, then treated with stannous chloride to precipitate sulfur,[5] and vacuum distilled from potassium hydroxide. A colorless liquid was collected. p-Methoxyaniline (J. T. Baker, practical grade) was purified by melting the crystals, then extracting with hot Skelly B. On cooling, light yellow, needle-shaped crystals were obtained. N-Benzylidenemethylamine (Aldrich Chemical Co.) was used without further purification.

Nitrogen from Air Products (high purity) was passed over copper wire heated to *ca.* 450° to remove oxygen.

Propylene carbonate solutions 0.1 F in tetraethylammonium perchlorate, *ca.* 5×10^{-4} or less in copper(II) perchlorate or in copper(I) perchlorate, and containing

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(2) B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J. Chem. Soc.*, 3215 (1961).

(3) A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 2974 (1961).
(4) M. L. Cluett, *Anal. Chem.*, **34**, 1491 (1962).
(5) A. I. Vogel, « Practical Organic Chemistry », 3rd ed., Longmans, Green and Co., Ltd., London, 1959, p. 563.

varying amounts of ligand were used in the polarographic study . The solutions were deoxygenated with nitrogen, which was presaturated with solvent, and protected from atmospheric oxygen during the course of measurement by passage of nitrogen over the surface. All solutions were examined at room temperature. Stock solutions of copper(I) perchlorate for the electrochemical studies were prepared either by the treatment of solutions of coppr(II) perchlorate (ca. $6 \times 10^{-4} F$) in propylene carbonate with copper wire at 75° overnight or by directly dissolving a suitable amount of tetrakis(acetonitrile)copper(I) perchlorate in propylene carbonate. Purified nitrogen presaturated with propylene carbonate was passed through the solutions continuously. Appropriate aliquot portions of these solutions were diluted to prepare the solutions for measurement.

Equipment. Current-voltage curves were recorded with a controlled potential polarograph of the type designed by Fisher, Kelley, and Jones[6,7] A three-compartment cell with glass frits of medium porosity separating the compartments was used. The dropping mercury electrode was placed in the central compartment, and the reference electrode (a saturated aqueous calomel) and the auxiliary electrode (platinum foil) were placed in the side arms.

Infrared spectra were obtained with a Perkin-Elmer Model 421 spectrophotometer. Free amines were examined as liquid films. The complexes were examind as films of the oils recovered on attempts to isolate the complexes or as Nujol mulls. A Cary Model 14 recording spectrophotometer was used for the visible spectral study. The visible spectra of oil-like products were obtained on films between two pieces of microscope slides. For highly oxygen sensitive products, high vacuum grease was used to seal the two glass plates before removing them from the dry bag. Reflectance spectral data in the visible region of the solid products were collected with a Beckman DU spectrophotometer with Reflectance Attachment 2580.

Preparation of Compounds. Copper(I)-Pyridine Complex. Tetrakis(acetonitrile)copper(I) perchlorate was treated in a nitrogen atmosphere with deaerated pyridine in a mole ratio of pyridine to copper(I) of slightly larger than 4:1. Displacement of acetonitrile took place rapidly. A stream of nitrogen was maintained over the mixture, contained in a round bottom flask, to sweep away the displaced acetonitrile and the excess pyridine. A light yellow product with a tinge of green was obtained. The copper content of the product was determined by the conventional iodometric method, after treatment of the complex with nitric acid. A value of 13.16% was found for the copper content of the product after passage of nitrogen over the sample for five hours. The product dried overnight was found to contain 13.24% copper. The theoretical value for the copper content of the sample Cu(C_5H_5N)$_4$ClO$_4$ is 13.28%. The five-hour drying period does not appear to be sufficient to remove all the excess pyridine.

(6) D. J. Fisher, M. T. Kelley, and H. C. Jones, *Anal. Chem.*, *31*, 1475 (1959).
(7) D. J. Fisher, M. T. Kelley, and H. C. Jones, *Anal. Chem.*, *32*, 1262 (1960).

Copper(I)Quinoline Complexes. The same preparative procedure as that used for the 4:1 pyridine-copper(I) complex was followed to obtain the perchlorate salt of the highest quinoline-copper(I) complex. The displacement of acetonitrile was likewise rapid, resulting in the formation of a yellow solution with some yellow crystals. The crystals, however, could not be completely dried even after ten days of passage of nitrogen over the sample. Treatment of the " wet " crystals with benzene yielded a yellow product which after washing with deoxygenated benzene and drying under nitrogen was 11.04% in copper, as determined by the conventional iodometric method, and 11.40% in copper, as determined by electrodeposition. The theoretical value for the copper content of the compound Cu(quinoline)$_3$ClO$_4$ is 11.54%.

Copper(I)-N-Benzylidenemethylamine Complexes. Tetrakis(acetonitrile)copper(I) perchlorate and deaerated N-benzylidenemethylamine were combined in a mole ratio of benzylidenemethylamine to copper(I) of slightly larger than 4:1. A stream of nitrogen was maintained over the sample, and after two days, a yellow solid was obtained. The copper content of the product was determined by electrodeposition, after decomposition of the complex with nitric acid. A value of 9.75% was found. When benzene was used to precipitate the complex, a much lighter yellow product was recovered, and increasing the extent of shaking and washing with benzene resulted in products with values of 11.94 and 14.37% for copper. The theoretical value for the copper content of the compound Cu(N-benzylidenemethylamine)$_4$ClO$_4$ is 9.93%; of Cu(N-benzylidenemethylamine)$_3$ClO$_4$, 12.21% and of Cu(N-benzylidenemethylamine)$_2$ClO$_4$, 15.83%.

To prepare the perchlorate salt of the highest isoquinoline-copper(I) complex, tetrakis(acetonitrile)copper(I) perchlorate was treated with isoquinoline as in the procedure above. In this case, only an oil-like product was obtained. All attempts to collect a solid product were unsuccessful. Difficulties also were encountered in obtaining solid samples of the highest n-butylamine-, piperidine-, and aniline-copper(I) complexes.

Results and Discussion

Polarography provides a rapid and simple means of determining the highest complex of a metal ion which undergoes reversible reduction at the dropping mercury electrode to give an amalgam. From the slope of the plot of the half-wave potential *vs.* the logarithm of the ligand concentration (Equation 1), where the ligand is in large excess, the

$$E_{1/2(c)} = E_{1/2(s)} - \frac{0.059}{n} \log \beta_p - p \frac{0.059}{n} \log C_L \qquad (1)$$

value of the ligand number, p, for the highest complex can be obtained. $E_{1/2(c)}$ and $E_{1/2(s)}$ are the half-wave potentials for the solutions containing the complexed and uncomplexed metal species, respectively, β_p is the overall stability constant of the complex with p ligands coordinated to the metal ion, and C_L is the

Table I. Data on Copper(I)(Monofunctional amine)$_p^+$ Complexes in Propylene Carbonate Obtained by Polarography [a]

Ligand	Ligand number of complexes, p [b]	β_p	Max. conc. of ligand, F
Pyridine	4	$10^{15.9\pm0.2}$	0.1
Quinoline	3	$10^{13.5\pm0.2}$	0.5
	2	$10^{12.4\pm0.2}$	
Isoquinoline	4	$10^{14.3\pm0.2}$	0.1
	3	$10^{13.3\pm0.2}$	
Piperidine	2	$10^{14.3\pm0.3}$	0.14
n-Butylamine	3	$10^{17.1\pm0.3}$	0.1
sec-Butylamine	2	$10^{16.4\pm0.3}$	0.1
Aniline	3	$10^{7.1\pm0.2}$	0.6
	2	$10^{6.5\pm0.2}$	
p-Methoxyaniline	3	$10^{9.0\pm0.2}$	0.8
	2	$10^{8.4\pm0.2}$	
N-Benzylidenemethylamine	3	$10^{12.9\pm0.2}$	0.5
	2	$10^{12.1\pm0.2}$	

[a] The $E_{1/4} - E_{3/4}$ values for the polarograms were in the general range of 60-65 mv. For a reversible one-electron process this value is 56 mv. [b] Obtained from the $E_{\frac{1}{2}Cu(I), Cu(Hg)}$ vs. $-\log C_{amine}$ plot. [c] Solutions were ca. 0.4 mM in copper(II) perchlorate or tetrakis(acetonitrile)copper(I) perchlorate. (Presence of acetonitrile did not alter the copper(I), copper(Hg) steep.).

bulk concentration of the ligand. Information on the monofunctional amine-copper(I) complex-formation systems examined is summarized in Table I. The calculations were based on equation 1. $E_{1/2(s)}$ was determined separately for each series of runs and ligands. These $E_{1/2(s)}$ values, corrected for overlap of the copper(II)/copper(I) and copper(I)/copper(Hg) steps, ranged from 0.400 to 0.425 V. β_p values were estimated by extrapolating the plots of $E_{\frac{1}{2}Cu(I), Cu(Hg)}$ vs. $-\log C_L$ to $-\log C_L = 0$ and using the $E_{1/2(s)}$ value for that series of runs.

Pyridine-Copper(I) System. The slope of 3.9×0.059 for the plot of $E_{\frac{1}{2}Cu(I), Cu(Hg)}$ vs. $-\log C_{pyridine}$ in the polarographic study denotes that the highest complex of pyridine and copper(I) ion in propylene carbonate is, as with nicotinamide and isonicotinamide,[1] the 4:1 species.

The solid salt tetrakis(pyridine)copper(I) perchlorate was obtained by displacement of the acetonitrile in tetrakis(acetonitrile)copper(I) perchlorate with pyridine. The infrared spectrum of the product (in Nujol mull) showed no bands in the C≡N and OH stretching regions, indicating that the replacement of acetonitrile was complete and no water or OH⁻ was present. Pertinent infrared data for tetrakis(pyridine)copper(I) perchlorate in the 1600 to 600 cm⁻¹ region have been summarized.[1] The infrared spectrum of coordinated pyridine has usually the following distinguishing features from that of the free base: (1) a weak band between 1235 and 1250 cm⁻¹, (2) a shift in the strong band at 1578 cm⁻¹ to 1600 cm⁻¹ (this band in the spectrum of the free base has a shoulder at 1593 cm⁻¹ which does not appear in the spectrum of coordinated pyridine or becomes degenerate with the 1625 cm⁻¹ band), and (3) shifts of the 601 and 403 cm⁻¹ bands to 625 and 420 cm⁻¹.[8] The spectrum of tetrakis(pyridine)copper(I) perchlorate has a weak band at 1227 cm⁻¹, a shift in the strong 1575 cm⁻¹ band to 1591 cm⁻¹, and a shift of the band at 598 cm⁻¹ for free pyridine to 616 cm⁻¹. Coordination of pyridine to copper(I) is quite evident.

The polarographic data and the information on the solid pyridine-copper(I) perchlorate definitely establish the formation of the complex species Cu(pyridine)$_4^+$.

The reflectance spectrum of a sample of tetrakis-(pyridine)copper(I) perchlorate in the visible region had a relatively strong broad absorption band with λ_{max} at ca. 390 nm and a broad band of low intensity at around 600 nm. The absorption at 600 nm is undoubtedly due to the presence of a copper(II) complex resulting from oxidation of a small amount of copper(I) during the spectral measurement. Pyridine has strong absorption bands at 250-260 nm but does not absorb in the visible region. The relatively strong band in the 360-420 nm region suggests that some type of charge transfer is involved in the complex system.

Quinoline-Copper(I) System. The polarographic study indicates that the principal copper(I) species over the range of 4×10^{-2} to $5 \times 10^{-1} F$ quinoline is the 3:1 complex. From 4×10^{-3} to $4 \times 10^{-2} F$ quinoline concentration, the plot of $E_{1/2}$ vs. $-\log C_{quinoline}$ assumes a slope close to 2×0.059, indicating the 2:1 complex to be the principal species in this range of quinoline concentration.

Solid tri(quinoline)copper(I) perchlorate prepared by mixing tetrakis(acetonitrile)copper(I) perchlorate and quinoline and treating the mixture with benzene showed no bands in the C≡N and OH stretching regions. The infrared data in the 1600-600 cm⁻¹ region of this salt are summarized below. The changes in the absorption bands for the complexed salt are indicative of coordination of quinoline to copper(I) ion.[9,10,11]

C-C stretching, Q: 1621, 1595, 1569, 1499, 1470, 1451, 1430; CuQ₄ClO₄: 1622, 1595, 1579, 1503, 1460, 1432; C-N stretching, Q: 1311; CuQ₄ClO₄: 1308; skeletal deformation in-plane, Q: 937; CuQ₄ClO₄: 947; ring breathing, Q: 781; CuQ₄ClO₄: 778 (Spectra of Q and CuQ₄ClO₄ obtained as Nujol mull. Band assignment based on literature information.[12])

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Because the conditions under which evidence for the formation of the 3:1 quinoline-copper(I) complex species was derived do not completely rule out the possibility of the formation of the 4:1 quinoline-copper(I) complex, a series of mixtures of exactly 3:1, 4:1, and 5:1 mole ratios of quinoline to tetrakis(acetonitrile)copper(I) perchlorate was prepared. In each situation, a yellow, viscous liquid was obtained. The higher the ratio of quinoline to copper(I), the deeper was the color of the mixture. The infrared spectra in the 4000-600 cm^{-1} region of these three preparations were obtained on thin film samples. Quinoline absorbs strongly at 1569 and 937 cm^{-1}, and the two bands shift to 1579 and 947 cm^{-1}, respectively, when the amine is involved in coordination. Uncoordinated quinoline in the mixtures, can be detected by the presence of these two bands. Examination of the bands at 1569 and 937 cm^{-1} of the three preparations indicated very weak absorptions for the 3:1 preparation and, importantly, a significantly larger increase in absorbance for one mole-ratio increment of increase of quinoline to copper(I) from the 4:1 to the 5:1 preparation than in going from the 3:1 to the 4:1 preparation. (See similar type data presented for the isoquinoline case in Figure 1). In addition, in the $C \equiv N$ stretching region, free nitrile bands at 2245 and 2285 cm^{-1} were observed. These bands were those of the acetonitrile molecules displaced from the coordination sphere of the starting copper(I) salt by quinoline. Significantly, the nitrile bands in the 2250 cm^{-1} region for the 3:1 preparation were not as well resolved as those for the 4:1 and 5:1 preparations. There was a small, but pronounced, shoulder on the higher frequency side of the 2245 cm^{-1} band indicative of coordinated nitrile. (Coordinated acetonitrile has absorption bands at 2270 and 2296 cm^{-1}). In going from the 3:1 to the 4:1 preparations, this coordinated acetonitrile was replaced by quinoline, and, therefore, well resolved free nitrile bands were observed for the 4:1 and 5:1 preparations. (See si-
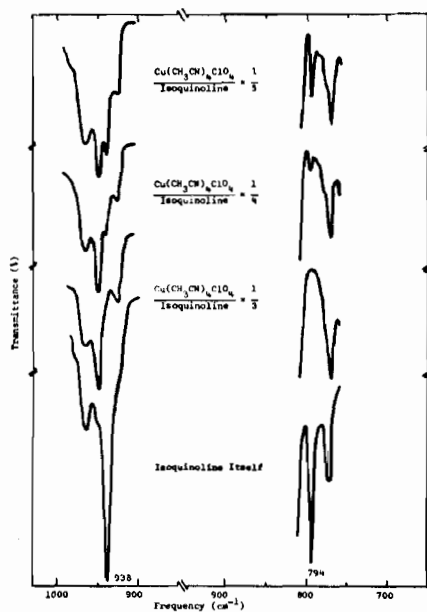
milar type data presented in Figure 2 for the isoquinoline case). From the above information, it is evident that a maximum coordination number of four can be reached for quinoline complexation of copper(I) ion.
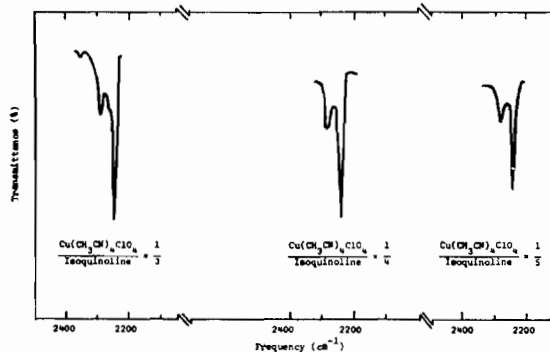

Figure 2. The Infrared Spectra of Copper(I) Complex of Isoquinoline in the $C \equiv N$ Stretching Region.

The visible spectrum of the oil-like product of 4:1 quinoline-copper(I) content and the reflectance spectrum of the solid 3:1 product obtained by precipitation from benzene were similar. Both products have relatively strong broad absorption bands in the 360-420 nm region with λ_{max} of 370 nm. The free ligand does not absorb in this region. A similar type of charge transfer as in the 4:1 pyridine-copper(I) complex is involved in these copper(I) complexes of quinoline.

Isoquinoline-Copper(I) System. From the polarographic study, over the range of 1×10^{-1} to $2.6 \times 10^{-1} F$ isoquinoline the 4:1 complex appears to be the principal copper(I) species, and from 4×10^{-3} to $1 \times 10^{-1} F$ isoquinoline, the 3:1 species is the principal complex.

When tetrakis(acetonitrile)copper(I) perchlorate was treated with isoquinoline, in a mole ratio of isoquinoline to copper(I) of slightly larger than 4:1, and nitrogen passed over the mixture, only a very viscous orange-yellow oil was obtained; no solid could be isolated from this mixture. The infrared spectra in the 1600-600 cm^{-1} region of free isoquinoline and the oil of 4:1 isoquinoline to copper(I) content are summarized below.

C–C and C–N ring stretching, IsoQ: 1625, 1586, 1572, 1495, 1457, 1428; Cu(isoQ)$_4$ClO$_4$: 1628, 1590, 1572, 1497, 1434; C–H bending, IsoQ: 1269, 1213; Cu(isoQ)$_4$ClO$_4$: 1273, 1207; unassigned, IsoQ: 938, 794, 630; Cu(isoQ)$_4$ClO$_4$: 948, 630, 615. (Spectral data collected on thin film samples. Literature data used for band assignment[13]).

A series of preparations of isoquinoline and tetrakis(acetonitrile) copper(I) perchlorate of 3:1, 4:1, and 5:1 mole ratios was made up as described for the quinoline system. The absorption bands at 938 and 794 cm^{-1} for free isoquinoline were used to detect the presence of uncoordinated isoquinoline in the mixtures. Comparison of the spectra of these three preparations at 938 cm^{-1}, 794 cm^{-1}, and, in the region

Figure 1. The Infrared Spectra of Copper(I) Complex of Isoquinoline at 938 and 794 cm^{-1}

(13) M. J. Lecomte, *C. R. Acad. Sci., Paris, Ser. B, 266*, 400 (1968).

2200-2300 cm^{-1}, for the free nitrile, leads to the same conclusion as in the polarographic study, four molecules of isoquinoline can coordinate to copper(I) ion. (See Figure 1 and 2).

The oil-like product of 4:1 isoquinoline to copper(I) content also has a relatively strong absorption band in the 360-420 nm region with λ_{max} at 370 nm. Pure isoquinoline is a colorless liquid and does not absorb in this region. Some type of charge transfer in the copper(I) complex is suggested.

Interestingly, coordination through the β position (isoquinoline) instead of the α position (quinoline) decreases steric hindrance in the coordination sphere sufficiently that tetracoordination of copper(I) by isoquinoline in propylene carbonate is attainable.

In these three heterocyclic aromatic amine cases, both the infrared data and the relatively strong absorption band in the 360-420 nm region of the copper(I) complexes are indicative of strong interaction between the copper atom and the aromatic amines involving d electrons of the metal and the empty π system of the heterocyclic bases. In the infrared, because of back bonding the fundamental frequencies of the pyridine nucleus are altered only slightly on coordination by copper(I),[8,14,15] whereas when pyridine is protonated or coordinated to BX₃ (X = H, F, Cl, or Br) owing to the absence of back bonding, there is marked change in the spectrum of pyridine.[8,15,16] The 360-420 nm absorption is a metal to ligand charge-transfer band.[17,18]

Piperidine-Copper(I) System. In the polarographic study of complex-formation between piperidine and copper(I), a value of two was calculated for the maximum number of piperidine coordinated to copper(I).

The piperidine-copper(I) system is very sensitive to oxygen. Treatment of tetrakis(acetonitrile)copper(I) perchlorate with deaerated piperidine in a mole ratio of 4:1 piperidine to copper(I) yielded a clear solution with a slight tinge of blue. Even in a nitrogen atmosphere, the blue color slowly intensified. Use of an argon atmosphere was found to decrease the problem of oxidation of copper(I). When argon was passed over a 4:1 mixture of piperidine and tetrakis(acetonitrile)copper(I) perchlorate for one day, the mixture turned viscous, but no solid was obtained. A value of 14.35% was found for the copper content of this viscous product. A composition of Cu(piperidine)$_{3.3}$ClO₄ is indicated. The less than 4:1 mole ratio of piperidine to copper(I) is the result of loss of piperidine owing to its volatility.

The infrared data in the 4000-600 cm^{-1} region of thin films of free piperidine and the oil-like product of 3.3 to 1 piperidine to copper(I) are: N–H stretching, Pip: 3280; Cu(pip)$_{3.3}$ ClO₄: 3320(sh), 3260(s); C–H stretching, Pip: 2920(s), 2840(s), 2790(s), 2720(s); Cu(pip)$_{3.3}$ClO₄: 2930(s), 2850(s), 2800(sh), 2730(sh); N–H deformation, Cu(pip)$_{3.3}$ClO₄: 1580; H–C–H bending, Pip: 1465, 1440; Cu(pip)$_{3.3}$ClO₄: 1450(b); H–C–H wagging, Pip: 1280(w), 1255(m);

Cu(pip)$_{3.3}$ClO₄: 1264(s); ring breathing, Pip: 933, 850; Cu(pip)$_{3.3}$ClO₄: 923, 860(s); H–C–C rocking, Cu(pip)$_{3.3}$ClO₄: 800(s). (Band assignment from literature information[16,19]).

Free piperidine has strong absorption bands at 2790 and 2720 cm^{-1}, attributed to C–H stretching vibration. These bands disappear almost completely when piperidine enters into coordination. The intensity of these two bands in the spectra of 3:1, 4:1, and 5:1 mole ratio mixtures of piperidine and tetrakis(acetonitrile)copper(I) perchlorate provides a rough measure of the amount of free ligand present in a sample. From the much larger increase in the absorbance at 2790, 2720, and 730 cm^{-1} for one mole ratio increment of increase of piperidine to copper(I) from the 4:1 to the 5:1 preparation than from the 3:1 to the 4:1 preparation, the possible tetracoordination of copper(I) by piperidine, suggested earlier by the 3.3 to 1 piperidine to copper(I) stoichiometry of the viscous product, is confirmed.

Importantly, tetrakis(piperidine)copper(I) ion has no absorption band in the 300-400 nm spectral region.

n-, sec-, and tert-Butylamine-Copper(I) System. In general, short chain aliphatic amines are very volatile and long chain aliphatic amines contribute toward steric and solubility problems. For this study of aliphatic amine coordination to copper(I) ion, a compromise selection of *n*-butylamine (b.p. 77.8°) was made, and to check on steric effects, *sec-* and *tert*-butylamine (b.p. 64 and 45°, respectively) were included. Polarographic studies of complex-formation involving these amines at high ligand concentrations, however, were not possible because of electrode fouling. In addition, the volatility of these amines, particularly the low boiling *tert*-butylamine, made the experimental work especially difficult.

In the polarographic study of *n*-butylamine-copper(I) complex-formation in propylene carbonate, a value of three was found for the ligand number of the highest complex. With solutions containing *sec*-butylamine, a maximum coordination of two was obtained for the highest *sec*-butylamine-copper(I) complex. The volatility of *tert*-butylamine prevented meaningful polarographic data to be collected for this butylamine-copper(I) complex-formation system.

Because of the gradual oxidation of copper(I) when tetrakis(acetonitrile) copper(I) perchlorate was treated with deaerated *n*-butylamine (1:4 mole ratio) in a nitrogen atmosphere, as indicated by the blue color of the solution, no solid salt of *n*-butylamine-copper(I) perchlorate was isolable.

The rapid examination of the liquid mixture obtained on combining *n*-butylamine with tetrakis(acetonitrile))copper(I) perchlorate as described above did not reveal an absorption band in the 300-400 nm spectral region.

Aniline- and p-Methoxyaniline-Copper(I) System. The basicity of aniline, the simplest aromatic amine, ($pK_b = 9.4$)[20] is much lower than that of aliphatic amines ($pK_b = 2$-3);[21] therefore, much weaker complexes would be expected. From polarographic study,

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β_3 and β_2 values of $10^{7.1}$ and $10^{6.5}$, respectively, were found. The 3:1 complex is the principal complex species over the range of *ca.* 2×10^{-1} to $6 \times 10^{-1} F$ aniline. From 5×10^{-2} to $2 \times 10^{-1} F$ aniline concentration, the plot of $E_{1/2}$ *vs.* $-\log C_{aniline}$ assumes a slope close to 2×0.059, indicating the 2:1 complex to be the principal species in this range of aniline concentration. The coordinating ability of aniline can be increased by having an electron donating group such as an alkoxy group in the *para* position. With solutions containg *p*-methoxyaniline, a value of 3 was obtained for p over the ligand concentration of 2×10^{-1} to $8 \times 10^{-1} F$. From 5×10^{-2} to $2 \times 10^{-1} F$ *p*-methoxyaniline concentration, the 2:1 complex was found to be the principal species. The constants β_3 and β_2 are $10^{9.0}$ and $10^{8.4}$, respectively. Although the stability of the complexes definitely increased, this does not lead to a higher *p*-methoxyaniline-copper(I) complex in propylene carbonate.

The rapid oxidation of copper(I) when tetrakis(acetonitrile)copper(I) perchlorate was treated with deaerated aniline in both the nitrogen and argon atmospheres used prevented isolation of a solid aniline-copper(I) salt.

N-Benzylidenemethylamine-Copper(I) System. The principal N-benzylidenemethylamine-copper(I) complex in propylene carbonate over the range of *ca.* 2×10^{-1} to $5 \times 10^{-1} F$ N-benzylidenemethylamine is the 3:1 species. Over the ligand concentration range of 5×10^{-2} to $2 \times 10^{-1} F$, the 2:1 complex is the principal species.

The solid obtained on mixing N-benzylidenemethylamine with tetrakis(acetonitrile)copper(I) perchlorate in a mole ratio of 4:1 and drying with nitrogen showed no infrared bands in the $C \equiv N$ and O–H stretching regions. The C=N frequency was shifted from 1655 cm^{-1} for the free ligand to 1632 cm^{-1} for the copper(I) complex. In addition to the coordinated C=N stretching band at 1632 cm^{-1}, there was a shoulder in the free C=N stretching region, *ca.* 10% in peak height of the band of the coordinated imine. The spectrum of a sample obtained by adding N-benzylidenemethylamine to the solid of 4:1 N-benzylidenemethylamine to copper(I) to make the final mole ratio of ligand to copper(I) equal to 5:1 showed that this added N-benzylidenemethylamine gave a much more intense band at 1655 cm^{-1} than observed in the 4:1 mixture. The fraction of free ligand in the 4:1 preparation is, therefore, quite small. Owing to the low volatility of the ligand (b.p. 183°), the small amount of excess ligand could not be swept away with nitrogen. The infrared spectrum of the solid product of 4:1 imine to copper(I) after treatment with benzene indicated absence of free ligand. Analysis of the copper content, however, revealed that 3:1 and 2:1 complexes were being obtained, depending on the vigor of the shaking and extent of washing with benzene.

The reflectance spectrum of tetrakis(N-benzylidenemethylamine)copper(I) perchlorate has a relatively strong broad absorption band in the 360-420 nm region with λ_{max} around 380 nm. It should be specially noted that the N-benzylidenemethylamine-copper(I) complex system is similar to those examined which contain the pyridine nucleus. Strong interaction of the d electrons of the copper atom with the empty π system of the aromatic ring occurs through the C=N bond, resulting in the yellow color of the tetrakis complex and contributing to the stability of the tetracoordinated species.