leaving groups is likely to be higher for Au(III) than Pt(II) irrespective of the number of chloride ions coordinated. If, as suggested by Basolo,[7] the main driving force for the reactions of gold(III) complexes is bond formation in the transition state, one must expect that the reactivity as well as the dependence of reactivity upon the basicity of the entering amine increases in going from Pt(II) to Au(III) complexes. The increase in reactivity, expressed as log (k_2^{Au}/k_2^{Pt}), is 2.15 for the weakest base, 4-cyanopyridine, and increases to 2.58 for the strongest base compared, 3,5-dimethylpyridine. At the same time the increase in the slope of the plot of log k_2 *vs.* pK_a is 2.75. Further investigations will be necessary in order to estimate the effect of the total charge of the complex upon the relationship between reactivity and basicity.

Experimental Section

Chloroauric acid was prepared starting from metallic gold with the usual method described in the literature. Methanolic solutions of $H[AuCl_4]$ follow Beer's law and no appreciable solvolysis is observed during the time necessary to follow the kinetics. Commercial pyridines were purified by distillation over potassium hydroxide pellets. Anhydrous methanol was prepared by distillation over $Mg(OCH_3)_2$. The products $[Au(am)Cl_3]$ were identified from the ultraviolet spectrum.[4]

Kinetics.—Methanolic solutions of chloroauric acid and of the amine were thermostated and mixed in the cell which was placed in the thermostated compartment of the spectrophotometer. The measurements were made by using a Optica-CF4 recording spectrophotometer, by scanning the near-ultraviolet spectrum from time to time in the course of the reaction. Some kinetic runs were made several times under the same conditions, and the rate constants were generally reproducible to better than 5%.

Acknowledgments.—We thank Professor A. Turco and Dr. M. L. Tobe for helpful and stimulating discussions.

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[7] F. Basolo, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 92.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Cyanide Complexes of Copper with Ammonia and Ethylenediamine[1]

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Complex cyanides of copper(I) are susceptible to oxidation by oxygen in the presence of ammonia or ethylenediamine if the $CN^-:Cu(I)$ ratio is less than 3. The stable products contain Cu(II) and Cu(I) in the ratio of 1:2. This was shown by stoichiometric analysis, by titration with NH_2OH_2Cl, and by magnetic susceptibility measurement. Crystalline samples of $Cu_3(NH_3)_4(CN)_4$ and $Cu_3(en)_2(CN)_4$ were prepared. Measurements of infrared and visible absorption spectra show that the N base is coordinated to Cu(II) as is also the Cu(I) cyano anion. In aqueous solution the cation–anion association persists for the ethylenediamine case. It dissociates on dilution, however. For the ammonia species, dissociation is complete even in saturated solution.

The formation of coordination compounds containing the cyanide ion is of great interest because of the possibility of π-bond formation between the metal ion and the ligand.[2] This possibility, along with the relative ease of observation of the C–N stretching frequency, has led to the use of cyanide ligands in investigations of mixed-ligand complexes. In some cases it has been found that the C–N frequency is sensitive to changes in the other ligands of a mixed (square-planar) complex.[3] An attempt to obtain information about this type of effect in a mixed-ligand complex with tetrahedral coordination involved an investigation of mixed complex formation with copper(I) cyanides.[4] It was found however that instead of mixed complex formation with copper(I), in the presence of N donors and air, the copper(I) was oxidized to a copper(II) species. Copper(I) cyanides are otherwise very stable toward oxidation of the metal (reaction with oxygen occurs at slightly elevated temperatures with the formation of copper(I) cyanate). The possibility of mixed complex formation with the copper(II) species exists. As stable complexes containing cyanide bound to copper(II) are unusual, it was thought that the oxidation and the product were deserving of further study. Infrared and visible spectroscopy provides information about the bonding in the copper(II) species, and the results with ammonia and with ethylenediamine (en) are presented here.

Experimental Section

Preparation of $Cu_3(NH_3)_4(CN)_4$. (a) From Copper(I) Cyanide.—Copper(I) cyanide was prepared by the method of Barber.[5] Sodium cyanide (0.25 mole) was dissolved in water (50 ml) and copper(I) cyanide (0.139 mole) was dissolved in the resulting solution. A 40% aqueous ammonia solution (20 ml) was added to the solution and a deep blue color formed within a few seconds, spreading downward from the exposed surface. The mixture was left for 48 hr to allow some of the ammonia

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[1] This work was supported by Grant G.P. 2643 from the National Science Foundation and presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

[3] J. M. Smith, L. M. Jones, L. K. Kressin, and R. A. Penneman, *Inorg. Chem.*, **4**, 369 (1965).

[4] D. Cooper and R. A. Plane, *ibid.*, **5**, 16 (1966).

[5] H. J. Barber, *J. Chem. Soc.*, 125 (1924).

to evaporate, after which time blue-green crystals of $Cu_3(NH_3)_4(CN)_4$ (0.01 mole, 7%) were collected from the solution. The crystals were washed successively with dilute aqueous ammonia, water, and acetone, and dried in a vacuum desiccator over phosphorus pentoxide.

(b) **From Copper(II) Sulfate.**—Copper(II) sulfate pentahydrate (0.1 mole) was dissolved in water (100 ml) and 40% aqueous ammonia was added until the initial precipitate completely dissolved. Sodium cyanide (0.2 mole) in water (50 ml) was added to the stirred copper–ammonia solution at room temperature and a precipitate of $Cu_3(NH_3)_4(CN)_4$ was formed immediately. The product (0.079 mole, 79%) was washed and dried as above. *Anal.* Calcd for $Cu_3(NH_3)_4(CN)_4$: Cu, 52.5; N, 30.8; CN, 28.7. Found: Cu, 51.8; N, 29.2; CN, 27.8.

Preparation of $Cu_3(en)_2(CN)_4$. (a) **From Copper(I) Cyanide.**—The compound may be prepared in a manner exactly analogous to that for $Cu_3(NH_3)_4(CN)_4$, but the product always exhibits an infrared absorption at 3550 cm^{-1} indicating the presence of water in the product.

(b) **From Copper(II) Sulfate.**—The method described by Gordon and Birdwhistell[6] for the preparation of $Cu(en)_2SO_4$ was used with modification. Two equivalents of sodium cyanide were added prior to precipitation by absolute ethyl alcohol. The first precipitate (of sodium sulfate) was removed by filtration and the solution was allowed to stand for 3 days, during which time the purple crystals of $Cu_3(en)_2(CN)_4$ separated. The product was washed with ethanol, dried at 120° for 24 hr, and stored in a vacuum desiccator. Infrared spectra of the crystals showed no lines attributable to sulfate ion. The compound may be recrystallized from 25% aqueous ethylenediamine but the spectrum shows an additional line at 3550 cm^{-1} due to water. The hydrate was not further examined. *Anal.* Calcd for $Cu_3(CN)_4(en)_2$: Cu, 46.0; N, 27.1; CN, 25.1. Found: Cu, 46.6; N, 27.2; CN, 24.6.

Analyses.—Some difficulty was encountered with the analyses of the complex cyanides dealt with in this work. In agreement with a report by Lock and Wilkinson,[7] it was found that standard microanalytical techniques were not reliable for complex cyanides of metals with a high affinity for cyanide. A preliminary investigation of the thermal decomposition of the ethylenediamine complex showed that, when heated to 300–400°, the solid black residue still contained some cyanide. The other products were ammonia, acetylene, and cyanogen. Standard microanalytical techniques were therefore abandoned. The method suggested by Heintz[8] and used successfully by Lock and Wilkinson[7] for cyanide complexes of ruthenium was tried. This involved the fusion of the complex with an excess of potassium metal and the gravimetric determination of cyanide as AgCN. This proved to be unsatisfactory; a qualitative test on the fusion products failed to indicate even the presence of cyanide groups, which were presumably still bound to the copper. The strength of the Cu–CN bond is also responsible for the failure of the nickel–EDTA method for determining cyanide described by Flaschka.[9]

The cyanide content of the complexes was determined by dissolving them in concentrated nitric acid and blowing a fast stream of nitrogen (through a fritted disk) through the boiling solution and then through a known volume of standard silver nitrate. The cyanide was then determined by adding a known volume of standard potassium chloride and back-titrating with silver nitrate, using a chromate indicator. Hydrolysis of the cyanide does not appear to be significant in this case. If, however, sulfuric acid is substituted for nitric acid, lower values are obtained, possibly owing to loss of cyanide through hydrolysis. The problem of cyanide hydrolysis was also important in the determination of total nitrogen using the Kjeldahl method. The values so obtained were always between the expected values for nitrogen from the N donor ligands and total nitrogen present, and the value varied depending on the length of time the sulfuric acid solution was boiled. The problem was overcome by using a catalyst of selenium dioxide to allow total conversion of the nitrogen present to ammonium sulfate. Total copper was determined spectrophotometrically by the method described by Vogel[10] after dissolution in concentrated nitric acid and boiling for 3 hr. The percentage of copper(II) present in the ammonia complex was determined by titrating spectrophotometrically using hydroxylamine hydrochloride.

Infrared spectra were recorded as KI pellets on Perkin-Elmer Models 337 and 521 grating spectrometers. Visible spectra were recorded on a Bausch and Lomb 505 recording spectrophotometer. Low-temperature visible spectra were recorded at −45° using conventional cells dipped in ethylene glycol to prevent fogging by condensation of atmospheric moisture. Visible spectra of solid samples were recorded on a Cary 14 spectrophotometer using KBr disks as normally pressed for infrared spectra. Raman spectra were recorded on a Cary Model 81 Raman spectrophotometer using the 4358-A line as the exciting line.

Results

Solutions of copper(I) cyanide in aqueous sodium cyanide exhibit distinct vibrational spectra for the two complex ions $Cu(CN)_4^{3-}$ and $Cu(CN)_3^{2-}$.[11] These solutions are stable toward oxygen, no change occurring when oxygen is bubbled through them. Conversely, copper(II) dicyanide is not stable but is reduced by the cyanide ion to a mixture of copper(I) cyanides (plus cyanogen). The tetracyanocuprate(II) ion is also known to be unstable at room temperatures.[12] No evidence was found for mixed-ligand complex formation between cyanides of copper(I) and σ donors,[4] but in the presence of air and within certain concentration limits nitrogen bases facilitated the rapid oxidation of the copper(I) species. The complete replacement of the cyanide groups by the nitrogen donors would be surprising in view of the fact that the cyanide ion replaces ammonia in the tetraamminecuprate(II) complex ion with the formation of tricyanocuprate(I). This could indicate the possible formation of a mixed-ligand complex. Previous investigators have reported no change in the position of the visible absorption band of both $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$ on the addition of cyanide ions,[13,14] and on this basis it was suggested that mixed complexes were not formed. Consequently, the oxidation of copper(I) cyanides in the presence of ammonia and of ethylenediamine was chosen for further study. In the following discussion oxidation refers to oxidation in the presence of air and *not* to an oxidation–reduction system independent of atmospheric oxygen.

In agreement with a study by Basset and Corbet[15] it was not possible to obtain solutions of the dicyanocuprate(I) alone, and at CN:Cu ratios of 3:1 it has been shown that the concentrations of species other than $Cu(CN)_3^{2-}$ are low.[16] Solutions with a CN:Cu ratio of 2.76:1 were oxidized (as observed by their

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[6] G. Gordon and R. K. Birdwhistell, *J. Am. Chem. Soc.*, **81**, 3567 (1959).

[7] C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.*, 2281 (1964).

[8] E. A. Heintz, *Inorg. Syn.*, **7**, 142 (1963).

[9] H. A. Flaschka, "E.D.T.A. Titrations," Pergamon Press Inc., New York, N. Y., 1959, p 59.

[10] A. J. Vogel, "Quantitative Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1961, p 824.

[11] M. J. Reisfeld and L. H. Jones, *J. Mol. Spectry.*, **18**, 222 (1965).

[12] R. Paterson and J. Bjerrum, *Acta Chem. Scand.*, **19**, 792 (1965).

[13] F. R. Duke and W. G. Courtney, *J. Phys. Chem.*, **56**, 19 (1952).

[14] S. Kida, *Bull. Chem. Soc. Japan*, **32**, 981 (1959).

[15] H. Basset and A. S. Corbet, *J. Chem. Soc.*, **125**, 1660 (1924).

[16] R. A. Penneman and L. H. Jones, *J. Chem. Phys.*, **24**, 293 (1956).

absorption in the visible region) within a few minutes of adding either ammonia or ethylenediamine. For solutions in which the CN:Cu ratio was increased to 3:1, the oxidation was not apparent until some 2–3 hr after the addition of the N donor, but oxidation was accelerated by bubbling gaseous oxygen through the system.

As the complex responsible for the blue color was separately isolated (see below), it was possible to estimate the percentage of the copper which had been oxidized in the original 3:1 ratio solution. This was done by comparing the optical density at $\lambda_{\max}$ in the visible region of a solution of known copper concentration with that of the 3:1 solution (also of known concentration) which had been exposed to an oxygen pressure of 20 torr above atmospheric for 24 hr. It was found that less than 1% of the copper(I) originally present could be accounted for as the copper(II) complex. The fact that solutions with CN:Cu ratios of 3.1:1 (plus N base) were not oxidized to an observable extent indicates that the ions $Cu(CN)_4^{3-}$ and $Cu(CN)_3^{2-}$ (which are observable in solution by their characteristic Raman spectra) are stable with respect to oxidation. The oxidizable species (containing less than three coordinated CN^-) must have low equilibrium concentrations at this ratio. As the CN:Cu ratio is decreased, however, oxidation occurs readily.

The crystals isolated from these oxidized solutions were found to have the empirical formulas $Cu_3(CN)_4(NH_3)_4$ and $Cu_3(CN)_4(en)_2$. They were moreover identical with those obtained by the addition of 2 equiv of cyanide per copper to solutions of $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$. The formation of these crystals was not reported by the workers previously cited,[13,14] possibly because they worked in higher concentrations of excess N-donor ligand in which the compounds are soluble. The formulas suggest that the compounds contain both copper(I) and copper(II). This is confirmed by the experiments described below.

The reduction of copper(II) salts by solutions of hydroxylamine hydrochloride is often used in the preparation of copper(I) complexes. As the products of the reaction do not absorb in the visible region, the percentage of copper(II) in the complex could be determined spectrophotometrically by titrating with standard hydroxylamine hydrochloride and observing the 600-mμ peak of the ammine complex. The value for the percentage of copper(II) obtained in this manner was only one-third of that obtained from a similar determination after boiling in concentrated nitric acid. This procedure could not be adopted for the ethylenediamine complex because the strongly bound ethylenediamine could not be displaced by the reducing agent and only the total copper percentage could be determined after oxidation as above.

The molar magnetic susceptibilities of the complexes were determined at 295°K using the Gouy method. Values obtained (neglecting any diamagnetic corrections for the ligands) were 522 and 582 $\times 10^{-6}$ cgs unit/mole for the ammonia and the en complex, respectively. Most copper(II) compounds have molar susceptibilities in the region 1100–1800 $\times 10^{-6}$ cgs unit/mole whereas copper(I) compounds are diamagnetic.[17] The values for the complexes are much too low for copper(II) compounds alone but are consistent with the formulation in which two-thirds of the copper is Cu(I). For the en complex, where only the total percentage copper could be determined, the similarity of the values of the magnetic susceptibilities indicates that this complex, like the ammonia complex, contains two Cu(I) atoms for each Cu(II).

Vibrational Spectra.—The infrared spectra of the complexes are compared with those of the corresponding solids containing the complex ions $Cu(NH_3)_4^{2+}$ and with ethylenediamine and NH_3 in Tables I and II.

TABLE I

INFRARED AND RAMAN SPECTRA OF $Cu_3(NH_3)_4(CN)_4$

$Cu_3(NH_3)_4(CN)_4$				
Infrared[a]	Raman[b]	Assignment	Cu-$(NH_3)_4^{2+}$ [c]	NH_3[c]
3325 m		NH_3 str	3270	3414
3250 m		NH_3 str		3312
3150 m		NH_3 str		
2130 s	2107	CN str		
2100 s	2098	CN str		
1610 m		NH_3 asym def	1596	1628
1262 s		NH_3 sym def	1245	950
1244 s				
1202 s				
680 m		NH_3 rock	709	

[a] KBr and KI pellets. [b] Solution in dilute aqueous ammonia. [c] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 149.

It is clear that considerable shifts are observed. While some degree of shifting or splitting of lines is expected in spectra of solid samples because of restraints imposed by the lattice, the shifts observed here are rather large for simple solid-state effects, particularly as the spectra for $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$ were obtained from solid samples. This indicates that the complex cations $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$ either are modified or are not present in the cyano complexes under discussion.

The Raman spectrum of the ammine complex was measured in the cyanide stretching region (2000–2300 cm^{-1}). The lines in other regions and the CN lines of the en complex were not sufficiently intense to be recorded. For the ammine complex two lines were observed at 2098 cm^{-1} depolarized and 2107 cm^{-1} polarized. Comparison with published data on complex copper(I) cyanides[11,18-22] shows that the lack of agreement between reported values makes it difficult to determine which complex gives rise to these lines.

Visible Spectra.—The visible spectra of the com-

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(17) "Tables Annuelles Internationales de Constantes et Donnees Numerique," Vol. 5, Section 7, Gauthier-Villars, Paris, 1957.

(18) G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **33**, 736 (1960).

(19) V. Lorenzelli and F. Gasmunco, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **35**, 524 (1963).

(20) G. Moreau, M. Poulet, and J. P. Mathieu, *Bull. Soc. Franc. Mineral. Crist.*, **88**, 6 (1955).

(21) L. M. Jones, *J. Chem. Phys.*, **29**, 363 (1958).

(22) P. Chiorboli and C. Testa, *Ann. Chim.* (Rome), **47**, 639 (1957).

TABLE II

INFRARED SPECTRUM OF $Cu_3(en)_2(CN)_4$

$Cu_3(en)_2(CN)_4$[a]	Assignment	$Cu(en)_2PtCl_6$[c]	en[d]
3295 s	NH_2 str	3320	3335
3260 m	NH_2 str		
3230 m	NH_2 str	3245	3246
3130 w	NH_2 str		
2940 w	CH_2 str		2930
2880 w	CH_2 str		2858
2095 s	CN str		
2080 s	CN str		
1605 w, sh	NH_2 scissor		1608
1575 s	NH_2 scissor	1571	1597
1450 w	CH_2 scissor	1475, 1463	1469, 1456
1374 vw	CH_2 wag	1376	
1315 vw	NH_2 wag	1321	1360
1275 w	CH_2 twist	1282	1305, 1298
1162 w	NH_2 wag	1166	
1089 m	*b*	1111 (1091?)	1104
1035 s	Skeletal en str	1044	1069
1018 m, sh	*b*	1017	
982 m	*b*		980
888 vw	CH_2 rock	889	772
878 vw	CH_2 rock		761
700 m	NH_2 rock	705	
690 m	NH_2 rock	694	
540 m	M–N str	538	
525 m	M–N str	523	
509 w	Skeletal bend[b]		648
470 w	Skeletal bend[b]		

[a] KBr and KI pellets. [b] Assignment not clear. [c] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17,** 68 (1961). [d] A. Sabatini and S. Califano, *ibid.*, **16,** 677 (1960).

plexes were recorded and compared with those of the corresponding complexes which contained no cyanide groups. For the ammonia complex $[Cu_3(NH_3)_4(CN)_4]$, the absorption in concentrated ammonia solution occurred at the same wavelength (610 mμ) and had the same extinction coefficient as $Cu(NH_3)_nSO_4$. For the ethylenediamine complex $[Cu_3(en)_2(CN)_3]$, however, the absorption was shifted to longer wavelength (584 mμ) compared to $Cu(en)_2SO_4$ (546 mμ) and showed almost double the extinction coefficient as shown in Figure 1. The same phenomenon may be observed by progressively adding cyanide to a solution of $Cu(NH_3)_nSO_4$ in concentrated ammonia solution or of $Cu(en)_2SO_4$ in 25% aqueous ethylenediamine solution. Previous workers[23] have studied the addition of cyanide ions to solutions containing $Cu(NH_3)_n{}^{2+}$ at pH 9, and a linear relationship between optical density and concentration of cyanide was found, with four cyanides per copper atom for complete reaction. For the cyanocuprate(I) complex under discussion, the maximum concentration should occur at two cyanides per copper atom (or six CN per three Cu, *i.e.*, two CN for reducing two copper atoms leaving four to form $Cu_2(CN)_4$), and the optical density should only be two-thirds that of the original solution. In order to reconcile this with the published data, the reaction was studied at pH 9, pH 10, and in concentrated ammonia (pH ~13). It was found that at high pH, less cyanide was necessary for complete reaction (Figure 2) and that in concentrated ammonia the optical density at two cyanides per copper was indeed one-third that of the original solution. In the case of the addition of cyanide to solutions of $Cu(en)_2{}^{2+}$ the wavelength shift and the intensity increase were not noted by previous workers.[14] The color change is however sufficiently clear to be visible to the naked eye.

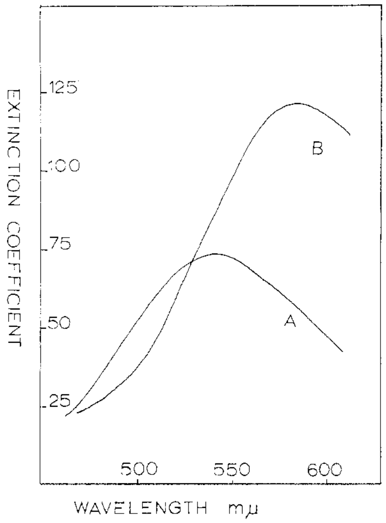

Figure 1.—Extinction curves for cupric complexes with ethylenediamine at 10^{-2} *M* in 25% aqueous ethylenediamine: A, $Cu(en)_2SO_4$; B, $Cu_3(en)_2(CN)_4$.

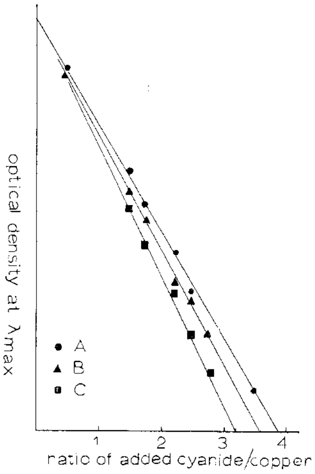

Figure 2.—The addition of cyanide to $Cu(NH_3)_4SO_4$ in aqueous solution: A, pH 9; B, pH 10; C, pH ~13.

It appears from these data that for the case of $Cu_3(NH_3)_4(CN)_4$, the cation has the same spectral characteristics in the visible region as $Cu(NH_3)_4{}^{2+}$. The infrared spectra of the two solid cyanocuprate complexes, however, indicate that the cation in both complexes is different from either $Cu(NH_3)_4{}^{2+}$ or $Cu(en)_2{}^{2+}$. In order to understand this, the visible spectrum of the ammonia complex $Cu_3(NH_3)_4(CN)_4$ was taken in the solid state, and the spectrum of $Cu(en)_2(CN)_4$ was taken at high dilution.

The visible absorption peaks for solid samples of $Cu_3(NH_3)_4(CN)_4$ and $Cu(NH_3)_4SO_4H_2O$ pressed in potassium bromide disks were at 630 ± 10 and 560 ± 18 mμ, respectively, as shown in Figure 3. The solution

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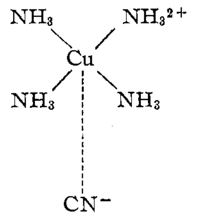
(23) R. K. McAlpine, *Anal. Chem.*, **25**, 331 (1953).

spectra (aqueous ammonia) for these two compounds are however identical. For the complex $Cu_3(en)_2(CN)_4$, satisfactory solid spectra could not be obtained, but at concentrations of 10^{-2} *M* a considerable shift from that of $Cu(en)^{2+}$ is observed as discussed above. Progressive dilution of a solution (aqueous ethylenediamine) of $Cu_3(en)_2(CN)_4$ from 10^{-2} to 10^{-4} *M* moved the absorption band at 584 mμ as shown in Figure 4.

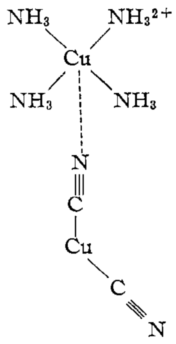
Discussion

The results presented here indicate that the complexes formed by oxidation of complex copper(I) cyanides in the presence of ammonia or of ethylenediamine contain copper in both the mono- and divalent states. It is known that copper(II) tetracyanide[12] is unstable at room temperature, so that the structures to be considered must involve copper(II) bound to the N donors with, or without, other coordinated cyanide groups. A square-planar copper(II) complex with one or more N-donor groups replaced by cyanide is improbable from the following considerations. The replacement of ligands in a square-planar complex by CN^- ligands with a higher ligand field strength is expected to shift the visible absorption band to higher energy. This is confirmed for the extreme case where all of the ligands are replaced as in $Cu(CN)_4^{2-}$ which at −45° in 60% aqueous methanol has an absorption at 530 mμ (compared to 620 and 560 mμ for $Cu(NH_3)_n^{2+}$ and $Cu(en)_2^{2+}$ in aqueous methanol). The observed shifts for the cyanocuprate(I) complexes dealt with in this work are in the wrong direction (lower frequency) for a mixed square-planar complex. On the other hand, coordination of a fifth N-base ligand[24] or CN^- [25] causes a shift to lower frequency as was observed for the present case.

The spectral data in the visible region suggest that, although the dilute solutions contain the ions $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$, in the solid state or in solutions of high concentration, association with some other species takes place. Two associated forms are considered, A and B.



A



B

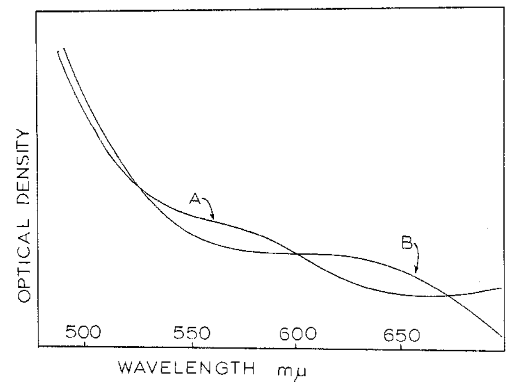


Figure 3.—Visible spectra of cupric complexes in KBr disks: A, $Cu(NH_3)_4SO_4$; B, $Cu_3(NH_3)_4(CN)_4$.

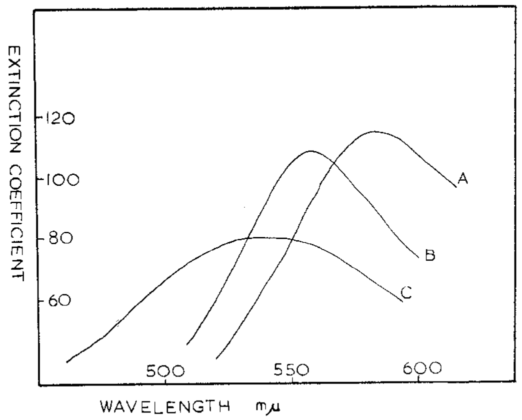


Figure 4.—Extinction curves for $Cu_3(en)_2(CN)_4$ in 5% aqueous ethylenediamine: A, 10^{-2} *M;* B, 10^{-3} *M;* C, 10^{-4} *M.*

A shift in the C–N stretching frequency, along with retention of the characteristic deep blue color of copper(II) complexes, has been presented in support of a Cu(II)–CN bond,[26] but this published work involving the solid-state combination of various Cu(II) complexes with cyanides can be interpreted in terms of structures similar to either A or B.

The work of Curtis and Curtis[25] has shown that the color change observed on adding cyanide (up to 10 moles per Cu) to solutions containing copper(II) bound to some tetradentate ligands is due to the formation of monocyanide adducts. The structure of the adducts is not discussed, but they presumably resemble A. The adducts, however, decompose over a period of a few hours, and, moreover, it is reported that the chemically less resistant noncyclic complexes are decomposed (to a copper(I) species) more rapidly. In fact, the addition of four or more cyanides per copper to solutions of $Cu(NH_3)_4^{2+}$ or $Cu(en)_2^{2+}$ causes decomposition within a few seconds at room temperature. The cyanocuprate(I) complexes $Cu_3(NH_3)_4(CN)_4$ and $Cu_3(en)_2(CN)_4$ are stable to decomposition both in the solid state and in solution. This stability would seem to indicate that the structure with bridging of the cyanide to the copper(II) ion *via* the nitrogen atom of the cyanide group (structure B) is more likely than the monocyano adduct of the type observed for copper(II) bound to tetradentate ligands (structure A).

Although high C–N frequencies are usually taken to indicate a bridging cyanide group, it is not clear that

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(24) J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

(25) Y. M. Curtis and N. F. Curtis, *Australian J. Chem.*, **18**, 1933 (1965).

(26) M. D. Glonek, M. R. Petra, and C. Curran, "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 412.

low frequencies necessarily indicate a nonbridging cyanide group. Indeed, the compound $KCu(CN)_2$, which is bridged *via* the nitrogen group,[27] has been reported to have C–N frequencies at 2085 and 2105 cm^{-1}.[19] The infrared data for potassium dicyanocuprate(I) have been confirmed by us, and therefore the low C–N frequencies observed for the cyanoamine complexes are not inconsistent with bridging of the type proposed. An X-ray study[27] has shown that the ion $Cu(CN)_2^-$ is angular in $KCu(CN)_2$, and if such is also the case for the complexes under discussion, bridging in the solid state would be expected to reduce the symmetry of the complex cation. This would explain the splittings and the shifts observed in the infrared spectra. Although the dicyanocuprate(I) ion is intuitively preferable as the anion, the vibrational spectra do not permit the distinction between this and the ion $Cu_2(CN)_4^{2-}$.

The visible data indicate that this bridging is retained for the ethylenediamine complex, in solutions at concentrations above 10^{-2} *M*, and that for the ammonia complex the bridging is not retained in solution. A possible explanation for this difference is the effect of the methylene groups attached to the coordinating nitrogen in the case of the ethylenediamine complex which is absent in the ammonia complex. The methylene groups would be expected to reduce the dielectric in the neighborhood of the cation and hence favor the association of the ion $Cu(CN)_2^-$ with $Cu(en)_2^{2+}$ as compared to $Cu(NH_3)_4^{2+}$. That the difference is not great is shown by the observation that, as the concentrations are decreased, dissociation occurs and an unmodified $Cu(en)_2^{2+}$ ion is observed in the absorption spectrum. It is concluded therefore that the complexes under discussion contain the ions $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$ and that under certain circumstances bridging can occur with the anion, probably $Cu(CN)_2^-$.

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Preparation and Electronic Spectra of Some Acidopentaammineiridium(III) Complexes

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A series of complex compounds of the type $[Ir^{III}(NH_3)_5X]Y_n$ has been prepared where X = I^-, Br^-, SCN^-, N_3^-, ONO^-, ^-OOCH, $^-OOCCH_3$, OH^-, ONO_2^-, H_2O, NCS^-, NO_2^- and Y = Cl^- or ClO_4^-, and their visible, ultraviolet, and infrared spectra were recorded. Assignment of the linkage isomers is possible on the basis of the spectrochemical series. The observed bands are interpreted as ligand field and electron-transfer transitions using common theoretical procedures. The infrared spectra, conductivity measurements, and molecular weight determinations furnish further evidence for the proposed complex formulation.

Introduction

The ultraviolet absorption bands of rhodium(III) pentaammine complexes were found[1] to follow closely the spectrochemical series established by Tsuchida.[2] The spectra of six-coordinated pentaammine d^6 complexes such as Co(III), Rh(III), and Ir(III) show only small deviations from octahedral symmetry at normal temperatures. For Co(III) complexes the low-symmetry component of the ligand field manifests itself[3] by a splitting of the first spin-allowed band $^1A_{1g} \rightarrow {}^1T_{1g}$. The second band does not seem to be affected, although according to the predictions of Yamatera[4] it should be split by the same amount. For the corresponding Rh(III) and Ir(III) compounds no term splittings can be detected,[1,5] but some show minor deviations from a Gaussian curve. It is therefore possible, in particular for the higher transition group ions, to classify the observed ligand field transitions according to term symbols of the octahedral group and define an approximate cubic ligand field parameter $\Delta = 10Dq$.[6] Instead of using the position of the first absorption band when establishing the spectrochemical series, as was originally done by Tsuchida,[2] we prefer to order the ligands according to their ligand field parameters Δ, since this classification eliminates various effects of electron interaction in the d shell and leaves the ligand field strength as a physical parameter describing the ligand–central atom interaction. The position of a molecular ligand in the spectrochemical series is, in general, determined by the atom attached to the central ion. We therefore expect ambidentate ligands to occupy different places in this series depending on the way they are linked to the central ion. It is therefore

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