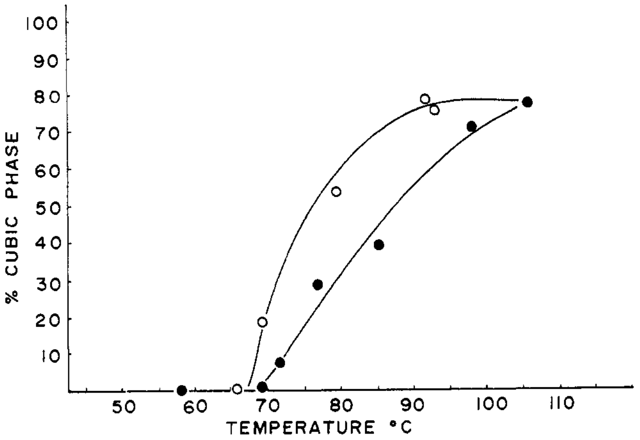

Figure 1.—Phase (cubic and tetragonal) composition as a function of temperature for $Cu(NH_3)_6Br_2$: solid circles, increasing temperature; open circles, decreasing temperature.

Elliott and Hathaway[4] suggested a structure in which the elongated tetragonal axes of the $Cu(NH_3)_6^{2+}$ group occur randomly along the *a* and *b* axes. This is clearly not the case, however, and, in fact, the large separation of the $Cu(NH_3)_6^{2+}$ ions precludes any significant short-range interaction between these ions. Thus, effects on the lattice parameters would be difficult to predict.

Although we cannot be certain of the source of the discrepancy, in the cases of the bromide and iodide, between this work and that of Peyronel[3] and Elliott and Hathaway,[4] it might well be that the latter workers failed to maintain equilibrium with ammonia gas at 1 atm. It is clear that the transition of $Cu(NH_3)_6Br_2$ to the cubic form is associated with considerable loss of ammonia. Ephraim[8] reported that the ratio of ammonia to copper in the bromide in equilibrium with 1 atm of ammonia is 5.48 at 65° and 5.08 at 115°. Permanent loss of ammonia might stabilize the high-temperature cubic phase. A thorough study of the phase transition as a function of ammonia pressure would probably clarify this situation, but such a study is beyond the scope of this report.

Among the possible causes of the irreversible nature of the phase transition are (1) slow diffusion of NH_3 in the solid and (2) stresses, produced by changes in the cell dimensions, which are not annealed out at the transition temperature. The evidence would seem to favor the latter as most important. In the first place, there is no detectable change in the cubic–tetragonal phase ratio over a period of hours once the steady value has been reached within a few minutes. Secondly, marked line broadening, particularly in the tetragonal phase, indicated considerable strain and/or reduction of particle size in the phase-transition region. For example, the line widths (2θ) at half-height for the (400) tetragonal line were 0.17 (normal), 0.29, 0.40, and 0.29° at temperatures of 45, 70, 81, and 92°, respectively.

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On the Question of Autoionization in Complexes of Metal Pentafluorides

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The possibility of ionization of complexes of phosphorus, arsenic, and antimony(V) fluorides with organic donor molecules was explored by nmr techniques. No evidence of ionization in acetonitrile solution was obtained at concentrations in the range 3–12 *M*. It was established that a hexacoordinate arsenic species such as $F_5AsNCCH_3$ hydrolyzes to give significant quantities of the AsF_6^- ion, presumably due to F^- attack of the complex in either an SN1 or SN2 type of mechanism.

In earlier work[1,2] we had characterized the complexes of phosphorus, arsenic, and antimony pentafluorides with organic donor molecules as hexacoordinate, monomolecular structures of C_{4v} symmetry. These conclusions were based on analyses of the F^{19} nmr spectra of acetonitrile solutions of the complexes. Recently, Kolditz and Rehak[3,3a] have proposed that in acetonitrile the complexes MF_5NCCH_3 (M = P, As, Sb) and $MF_5N(CH_3)_3$ (M = P, Sb) undergo significant autoionization

$$2MF_5\cdot\text{donor} \rightleftarrows MF_4(\text{donor})_2^+ + MF_6^-$$

Conductivity data and hydrolysis studies comprise the experimental basis of their proposal. We wish to confirm our original observations and conclusions and to raise serious question regarding the proposal of Kolditz and Rehak.

As originally reported,[1] the F^{19} spectrum of $F_5PN(CH_3)_3$ in acetonitrile solution consists of two doublets

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[1] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

[2] E. L. Muetterties, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 513.

[3] L. Kolditz and W. Rehak, *Z. Anorg. Allgem. Chem.*, **342**, 32 (1966).

[3a] NOTE ADDED IN PROOF.—Professor Kolditz in a personal communication to us has made the valid point that the concentration ranges examined conductometrically in his work[3] are lower (~10^2 to 10^3) than those employed in these nmr studies. Professor Kolditz has, however, reexamined these systems and is now obtaining conductivities significantly lower than those published originally.[3]

and two quintuplets.[4] This is consistent only with C_{4v} symmetry for the arrangement of fluorine atoms. There are no extraneous fluorine resonances provided the reagents and solvent are rigorously dried and transferred in a vacuum system and the complex is carefully purified by vacuum sublimation (the complex is hydrolyzed on exposure to the atmosphere). If these experimental conditions are not observed, the F^{19} spectrum of the solution has, in addition to the resonances described above for the complex, a doublet that arises from hexafluorophosphate ion.[5] We found that omission of the sublimation step yields solutions that contain up to 10% hexafluorophosphate ion. We also established by nmr studies that hydrolysis of the complex in solution yields the hexafluorophosphate ion. Hydrolysis was achieved by exposure of the solution to the atmosphere and by addition of moist acetonitrile to the solution. The rate of hydrolysis is relatively low at 25° and very high at 80°.

Koldtiz and Rehak report the molar conductivity of $F_5PN(CH_3)_3$ in acetonitrile (10^{-2} *M*) to be comparable to that of inorganic salts in acetonitrile. The implication is that extensive autoionization occurs. This, however, cannot be the case. The nmr data unequivocally establish that no more than 1% of $F_5PN(CH_3)_3$, if any at all, is dissociated into ions in acetonitrile solution. Furthermore, there can be no labile equilibrium between $F_5PN(CH_3)_3$ and ions of the type $F_4P[N(CH_3)_3]_2^+$ and PF_6^-, if these exist, in acetonitrile solution because the F^{19} nmr spectrum of the solution is temperature insensitive over the temperature range of about -60 to $+80°$. There is essentially no broadening of the individual peaks suggestive of exchange which is, of course, inherent in an autoionization and which we believe should be a fast process *in solution*.[6] There is no apparent dependence of spectral characteristics with time, *i.e.*, at least over a period of days.

We reconfirm our observation that the F^{19} nmr spectrum for F_5PNCCH_3 is a doublet ($J_{PF} = 770$ cps) at 25° and at temperatures substantially above 25°. Kolditz and Rehak incorrectly quote us[1] as reporting this spectrum as a broad single peak at room temperature. We find a single broad F^{19} resonance for acetonitrile solutions of phosphorus pentafluoride only when gross amounts of $(n\text{-}C_3H_7)_4N^+PF_6^-$ are added to the solution. The doublet F^{19} resonance of the phosphorus pentafluoride solutions in acetonitrile does collapse at about +80° to a very broad peak. We ascribe this collapse not to autoionization but to the presence of trace hexafluorophosphate ion impurity. This P–F bond-breaking process is visualized as

$$F^- + PF_5 \xrightarrow{\text{very fast}} PF_6^- \tag{1}$$

$$F_5PNCCH_3 \overset{\text{fast}}{\rightleftharpoons} F_5P + NCCH_3 \tag{2}$$

$$F_5P + PF_6^- \underset{\text{determining}}{\overset{\text{rate}}{\rightleftharpoons}} PF_6^- + PF_5 \tag{3}$$

That (2) is faster than (3) is clearly illustrated in the low-temperature ($\sim -60°$) spectrum of F_5PNCCH_3–$(n\text{-}C_3H_7)_4N^+PF_6^-$ mixtures where the PF_6^- resonance and the doublet F_5PNCCH_3 resonance are clearly discernible; these separate resonances broaden and merge into a single doublet on warming to 25°.

Kolditz and Rehak report for arsenic pentafluoride a molar conductivity in acetonitrile that is the same order of magnitude as Λ_0 for sodium iodide and tetraethylammonium chloride in this solvent. They also report that hydrolysis of the acetonitrile solution of arsenic pentafluoride yields half of the arsenic as arsenate and half as hexafluoroarsenate ion. The implication is that the complex is essentially completely ionized into the $AsF_4(NCCH_3)_2^+$ cation and the AsF_6^- anion. In one of our earlier papers[2] we described the nmr data for the arsenic pentafluoride–pyridine complex; the spectrum is consistent only with a six-coordinate complex with a C_{4v} arrangement of fluorine atoms. In our earlier investigation we did not examine the acetonitrile complex of arsenic pentafluoride. We now find that the F^{19} nmr spectrum of acetonitrile solutions of arsenic pentafluoride consists solely of a doublet and a quintuplet of relative intensities 4 and 1, respectively, which can be explained only in terms of a six-coordinate complex.[7] These data clearly establish that there is no significant amount of ionic species present in acetonitrile solutions of arsenic pentafluoride. We have no simple rationalization for the very high conductivity of these solutions as reported by Kolditz and Rehak. It is possible, particularly considering the hydrolytic sensitivity of the complexes and the low concentrations employed in the conductivity studies, that the observed conductivity was characteristic of a partially hydrolyzed solution. We do have a rigorous explanation for Kolditz and Rehak's observations on the hydrolysis of the complex. The hexafluoroarsenate anion is not present in the original solution but is produced on hydrolysis either with water or with aqueous base. This was followed by nmr spectroscopy simply by adding water or aqueous base to the acetonitrile solution of arsenic pentafluoride. The addition of water or base leads to a decrease in the intensity of the resonances associated with the octa-

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[4] The J_{PF} and δ values are 836 cps and +72.2 ppm for the four basal fluorine atoms and 731 cps and +82.8 ppm (fluorotrichloromethane external reference) for the apex fluorine atom. The FF coupling constant is 51 cps. The doublets and quintuplets are slightly distorted for the AB_4 system, with $\delta_A - \delta_B$ only an order of magnitude larger than *J*; perturbations are in explicit accord with theoretical calculations.

[5] The hexafluorophosphate ion resonance in acetonitrile is very sharp and can be detected at levels that are less than 0.5% those of $F_5PN(CH_3)_3$ in a saturated solution of the complex.

[6] This same observation pertaining to temperature insensitivity also extends to solutions containing $F_5PN(CH_3)_3$ and $(CH_3)_3NH^+PF_6^-$ although at elevated temperatures there is a slight but discernible increase in line widths for the resonances associated with the octahedral complex.

[7] The chemical shifts for the basal and apical fluorine atoms are +41.0 and +82.7 ppm (fluorotrichloromethane internal reference) and the F–F coupling constant is 115 cps. It is of interest to note that in this particular complex As–F coupling is absent whereas a large As–F coupling of about 995 cps was observed for the pyridine[2] complex. Apparently in the case of the acetonitrile complex the field gradient about the arsenic is sufficiently large that there is a high rate of quadrupole relaxation which effectively decouples the arsenic and fluorine nuclei. It would appear then that these AsF_6 complexes provide a very sensitive probe for field gradient about the arsenic nucleus. We plan to explore this spectral aspect of arsenic pentafluoride complexes in more detail.

hedral complex and the appearance of a four-line pattern which is due to the hexafluoroarsenate anion.[8] On complete hydrolysis, the only arsenic fluoride species discernible in solution is the hexafluoroarsenate anion. Thus, the Kolditz and Rehak experiments on hydrolysis bear no relation to the species originally present in solution.

Kolditz and Rehak report for the antimony pentafluoride–acetonitrile complex a conductivity in acetonitrile that is an order of magnitude lower than that of the corresponding arsenic pentafluoride complex. We find that the F^{19} nmr spectrum of this particular complex in acetonitrile solution is a two-line pattern of relative intensities 4 and 1 consistent with an octahedral complex. Failure to resolve any F–F coupling[9] may be due either to exchange that could be catalyzed by impurities[10] or to an intermediate case of quadrupole relaxation. In any case, the spectral data give no evidence of ionic species as postulated by Kolditz and Rehak.

Autoionization in the group Va pentafluorides is a subject of considerable interest to us,[11] but to date we find no convincing evidence that such processes occur to any significant extent in these pentafluorides or in organophosphorus(V) fluorides.

Experimental Section

Reagent and Solvent Purification.—Acetonitrile was purified by a technique developed by Dr. J. S. Fok of these laboratories. All purification steps were performed in an atmosphere of nitrogen and glassware was vacuum dried at elevated temperatures. Eastman Anhydrous acetonitrile, catalog No. X488, was shaken overnight with 100 g of Woelm basic alumina/l. of solvent. The solvent was decanted over dry glass wool, shaken with 2 g of phosphorus pentoxide/l., and then decanted into a distillation flask containing 1 g of phosphorus pentoxide/l. of solvent. The conductivity of the acetonitrile distillate was continuously monitored, and collection was made when the conductivity reached 1.5×10^{-7} ohm^{-1} cm^{-1}. (Kolditz and Rehak[3] report a conductivity for their acetonitrile of 1.5×10^{-8} ohm^{-1} cm^{-1}.) The purified acetonitrile was finally distilled into the reaction vessel or nmr tube from phosphorus pentoxide in a vacuum system. An alternative sample of acetonitrile, containing 0.086% water (determined by the Karl Fischer method), was used for some experiments. Toluene, Fisher Certified reagent grade, was refluxed and then distilled in the presence of calcium hydride into a storage flask containing calcium hydride. Further transfer of the solvent was carried out under vacuum. Trimethylamine was stored at room temperature in the presence of lithium aluminum hydride until hydrogen evolution had ceased and was subsequently handled under vacuum. Phosphorus pentafluoride was purified in a vacuum system by twice passing the gas through a U tube maintained at −112° to a U tube at −138°. The infrared spectrum of the purified material indicated the presence of phosphorus oxyfluoride and phosphorus trifluoride in only trace amounts. Arsenic pentafluoride and antimony pentafluoride were each fractionally distilled at atmospheric pressure.

Sample Preparation and Spectra.—Unless otherwise stated, all operations were caried out under vacuum. Samples were stored in sealed nmr tubes at liquid nitrogen temperatures. High-resolution F^{19} nuclear magnetic resonance (nmr) spectra were obtained with either a Varian Associates A-56 or an HR-60 instrument operating at 56.4 Mc/sec. Chemical shifts are referenced to fluorotrichloromethane.

$F_5PN(CH_3)_3$.—Purified toluene, about 10 ml, and trimethylamine, 1.39 mmoles, were transferred to a U tube with an attached nmr sample tube. The solution was warmed to −30° and 1.39 mmoles of gaseous phosphorus pentafluoride was admitted. After completion of the reaction and removal of toluene by distillation, the pale yellow solid was washed into the nmr sample tube with 0.4 ml of acetonitrile (0.086% water). The F^{19} spectrum contained only resonances assignable to $F_5PN(CH_3)_3$ and to the hexafluorophosphate ion (J_{PF} = 708 cps; δ = +72.6 ppm, external standard). The hexafluorophosphate ion was presumably present as the trimethylammonium salt. Integration of peak areas indicated the presence of $F_5PN(CH_3)_3$ and hexafluorophosphate in a ratio of 9:1. In a second experiment in which conductivity grade acetonitrile was employed as solvent, the percentage of hexafluorophosphate was smaller. After removal of toluene, acetonitrile was condensed into the U tube and allowed to warm in the presence of the product. This acetonitrile was distilled, and approximately half of the product was sublimed at 50° under high vacuum into an nmr tube. The remaining product was washed with a separate portion of conductivity grade acetonitrile into a second tube. The nmr spectrum of the sublimed product contained peaks assignable only to $F_5PN(CH_3)_3$; no hexafluorophosphate was detected. The unsublimed portion contained 3% hexafluorophosphate in addition to $F_5PN(CH_3)_3$.

The spectrum of a sublimed sample of $F_5PN(CH_3)_3$ dissolved in acetonitrile remained essentially constant over a temperature range of about −60 to 85°. The half-height width of the peak appearing at lowest field in the spectrum (*i.e.*, the low-field portion of the 51-cps doublet) was 16 cps at room temperature and 18 cps at 85°.

Hydrolysis experiments were carried out on the samples after examination of the spectra. A sample of $F_5PN(CH_3)_3$ containing 10% trimethylammonium hexafluorophosphate in acetonitrile was exposed to the air until the solvent had evaporated. The nmr spectrum of the resulting solid (redissolved in acetonitrile) indicated an increase in the quantity of PF_6^- to 33%. When this solution was warmed to 80° a rapid reaction took place in which the remaining $F_5PN(CH_3)_3$ was hydrolyzed and PF_6^- was the sole phosphorus fluoride remaining in solution. The hexafluorophosphate ion was also generated by addition of 10% water–90% acetonitrile solutions to the sample tubes.

The melting point of a sublimed sample of $F_5PN(CH_3)_3$ (previously reported through typographical error as 214–215°[1]) was redetermined as 148°.

F_5PNCCH_3.—The F_5PNCCH_3 complex was prepared in varying states of purity by slowly warming mixtures of phosphorus pentafluoride (1.4 mmoles) and excess acetonitrile (0.4 ml) from −196° to room temperature. The solution of the complex prepared with conductivity grade acetonitrile was pale yellow. The solvent and complex were distilled under vacuum from an essentially nonvolatile yellow impurity into the nmr tube to yield a very pale yellow solution (I).[12] A yellow solution of 1.36 mmoles of F_5PNCCH_3 prepared in 0.4 ml of acetonitrile containing 0.086% water (II) and a similar solution to which 0.254 mmole of tetra-*n*-propylammonium hexafluorophosphate had been added (III) were examined without further purification. The spectra of solutions I, II, and III at 85° each consisted of a singlet of half-height peak widths 230, 90, and 30 cps, respectively. At room temperature the spectra of I (δ = +59.6 ppm) and II each consisted of a doublet with individual member widths of 75 and 140 cps, respectively, and the spectrum of III consisted of a singlet of width 350 cps. The doublet character of I and II

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[8] K. J. Packer and E. L. Muetterties, *Proc. Chem. Soc.*, 147 (1964). AsF_6^- was identified by δ_F and J_{AsF} values in this solvent and by isolation and analysis of the $(n\text{-}C_3H_7)_4N^+$ salt.

[9] This coupling is observable in other antimony pentafluoride complexes.[2]

[10] We did not devise a satisfactory purification procedure for this acetonitrile complex.

[11] E. L. Muetterties and W. Mahler, *Inorg. Chem.*, **4**, 119 (1965).

[12] Some of the solutions were colorless initially and then colored on standing. The reverse color change was also observed. We have no explanations for these changes. Coloration did not correlate with nmr spectral changes.

was maintained to the freezing points of the solutions (about −60°) with the peak widths of I consistently smaller than those of II. As the temperature of III was progressively lowered from room temperature, the signal first broadened and then emerged at about −40° as two doublets characteristic of F_5PNCCH_3 and the hexafluorophosphate ion.

After 0.05 ml of 10% aqueous acetonitrile was added to I, the spectrum of the solution at room temperature consisted of a doublet (half-height width about 340 cps), very much broadened with respect to the doublet obtained from the anhydrous sample.

$F_5AsNCCH_3$.—The $F_5AsNCCH_3$ complex was prepared by warming mixtures of AsF_5 and conductivity grade acetonitrile from −196° to room temperature. Spectra were obtained from saturated acetonitrile solutions (yellow coloration) of the sublimed complex and consisted solely of a doublet and quintuplet of relative intensities 4.0 and 0.98, respectively. The relative sensitivities of the HR-60 and A-56 nmr instruments are such that the quintuplet was clearly visible only in spectra obtained with the HR instrument.

The spectrum of a hydrolyzed $F_5AsNCCH_3$ solution generated by addition of 0.25 ml of 30% aqueous acetonitrile to 1.27 mmoles of $F_5AsNCCH_3$ in 0.4 ml of acetonitrile had the quartet typical of the AsF_6^- ion[8] with peak positions at 2270, 3155, 4115, and 5020 cps to high field of the internal reference. The spectrum of a solution of similar solvent composition, containing 1.30 mmoles of potassium hexafluoroarsenate in 0.6 ml of solvent, exhibited peaks at 2257, 3170, 4117, and 5025 cps. The spectrum of a hydrolyzed $F_5AsNCCH_3$ solution generated by addition of an acetonitrile solution of $F_5AsNCCH_3$ (1.9 mmoles) to 0.4 ml of 25% sodium hydroxide in water also contained peaks characteristic of the hexafluoroarsenate ion.

$F_5SbNCCH_3$.—Acetonitrile, 0.4 ml, conductivity grade, was distilled into an nmr tube containing approximately 0.6 g (3 mmoles) of antimony pentafluoride. The mixture was warmed slowly to room temperature. The spectrum of the saturated solution, obtained with the HR-60 instrument, contained two broad singlets of relative intensities 4.0 and 1.14 appearing at +108 and +139 ppm from the internal standard.

Contribution from the Departments of Chemistry and Chemical Engineering,
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Thermodynamics of Metal Cyanide Coordination. VI. Copper(I)- and Silver(I)-Cyanide Systems[1a]

By Reed M. Izatt,[1b] H. Dee Johnston, Gerald D. Watt,[1c] and James J. Christensen[1b]

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Log K, $\Delta H°$, and $\Delta S°$ values reported for the consecutive interaction of CN^- with $Cu(CN)_2^-$ to form $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ are: $\log K = 5.30, 1.5$; $\Delta H° = -11.1, -11.2$ kcal/mole; and $\Delta S° = -13.4, -31$ cal/deg mole, respectively. Values of $\Delta H°$ and $\Delta S°$ for the formation of $Ag(CN)_3^{2-}$ from $Ag(CN)_2^-$ and CN^- are determined to be −0.6 kcal/mole and +5 cal/deg mole, respectively. Also, $\Delta H°$ and $\Delta S°$ values reported for the reaction $M^+ + 2CN^- = M(CN)_2^-$ (M = Cu, Ag) are: $\Delta H° = -29.1$ and -32.1 kcal/mole and $\Delta S° = +12$ and -16 cal/deg mole, respectively. The data are compared with those previously reported for the Zn^{2+}–CN^- system.

Introduction

Previous papers in this series have reported thermodynamic values for the interaction of CN^- with Ni^{2+} [2] and Zn^{2+}.[3] Two significant observations made in these studies concerning consecutive species intermediate between M^{2+} and $M(CN)_4^{2-}$ (M = Ni, Zn) were (1) that such species did not exist in detectable concentrations in the Ni^{2+}–CN^- system and (2) that, except for $ZnCN^+$, they were present in the Zn^{2+}–CN^- system. The $\Delta S°$ values for the formation of the $M(CN)_4^{2-}$ species from M^{2+} and CN^- were found to be nearly identical and very small for the two systems. Thus $\Delta G°$ (log K) is proportional to $\Delta H°$ in both systems but is much smaller (−26.77 *vs.* −41.1 kcal/mole) in the case of the Zn^{2+}–CN^- system.

Cuprous ion is isoelectronic with Zn^{2+} making a thermodynamic study of the Cu^+–CN^- system of interest in order to be able to compare the results with those of the corresponding Zn^{2+}–CN^- system. In addition, a knowledge of the thermodynamic quantities provides the necessary information to learn the relative importance of $\Delta H°$ and $\Delta S°$ in determining the stabilities of the species involved. Inclusion of Ag^+ in the study should contribute information on the effect of changing from the first to second transition series in d^{10} ions where ligand field effects are absent.

The species formed when CN^- interacts with Cu^+ have been identified by Cooper and Plane[4] and Penneman and Jones[5] to be $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$. Earlier spectral studies of the Cu^+–CN^- system have been summarized by Cooper and Plane.[4] Evidence based on infrared studies for corresponding complexes in the Ag^+–CN^- system has been reported by Jones and Penneman.[6] Equilibrium constant data valid at 25° and ionic strength $\mu = 0$ have been reported and previous work has been summarized for the

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[2] J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, *Inorg. Chem.*, **2**, 337 (1963).

[3] R. M. Izatt, J. J. Christensen, J. W. Hansen, and G. D. Watt, *ibid.*, **4**, 718 (1965).

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

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

[6] L. H. Jones and R. A. Penneman, *ibid.*, **22**, 965 (1954).