[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Interaction of Metal Ions with Heterocyclic Amines. Silver(I) Complexes

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A series of solid silver(I)–heterocyclic amine compounds was prepared and characterized. Absorption data were obtained in the ultraviolet and in the infrared regions of the spectrum. Relative stability values were determined in acetonitrile and in ethanol at 20°. Basicity values for 2,2′-bipyridine, 2,2′-biquinoline and 1,10-phenanthroline in aqueous ethanolic solutions are reported.

Introduction

Crystalline compounds formed by the interaction of the silver(I) ion and heterocyclic amines have long been known. Coördination compounds of pyridine,[2] quinoline[3] and 1,10-phenanthroline[4] have been prepared and isolated. The interaction of silver with methyl substituted pyridines and quinolines also has been observed, but solid compounds rarely have been prepared. Studies in solution have been limited to a few investigations of ligand association with the metal ion through solubility,[5] electromotive force[6,7] and absorption measurements.[8]

The behavior of silver heterocyclic amine compounds in solution usually has been correlated with that for silver amine compounds. Partly as a result, attempts to relate the strength of the silver–nitrogen bond to the electron density on the nitrogen atom have led to diverse conclusions. One group of workers has reported that no relationship exists between the base strength of the amine and the stability of silver compounds,[5] another group has found a proportionality between the two factors,[6] and still another has reported a dualistic dependence of stability upon basicity and ligand structure.[7]

In view of the above situation, it became of interest to investigate a large number of silver(I) coördination compounds. The interaction of some thirty amines with silver nitrate was studied. The compositions of the solid compounds were ascertained and stability data in acetonitrile and in ethanol determined. Absorption data in the ultraviolet and infrared regions of the spectrum were also obtained for certain of the compounds.

Experimental Part

Reagents.—The 2,2′-bipyridine, 2,2′-biquinoline and 1,10-phenanthroline were obtained from the G. Frederick Smith Chemical Company and were used as received. The 3-methylisoquinoline was obtained, in pure form, from the Fluka Chemical Company. The 2-aminopyridine was obtained from the Reilly Tar and Chemicals Corp. and was used as received. Student preparations from this Laboratory were the source of purified 4,8-dimethylquinoline, 6-methoxylepidine and 4,4′-bipyridine. These several amines were obtained from the Aldrich Chemical Company: 7-methylquinoline, 2,4-dimethylquinoline, 2-cyanopyridine, 4-cyanopyridine, 2-chloropyridine, 2-chloroquinoline, 4,7-dichloroquinoline, 3-bromoquinoline, 5-nitroquinoline and 5-nitroisoquinoline. These reagents were redistilled or recrystallized from ethanol before use. All other heterocyclic amine reagents were obtained from the Eastman Kodak Chemical Company and were redistilled or recrystallized from ethanol before use.

Acetonitrile was obtained from the Matheson Coleman and Bell Division of the Matheson Company, and was purified by standard methods.[9] Other organic solvents were redistilled before use. All other chemicals were of reagent grade quality.

Preparation and Analysis of Silver–Amine Compounds.—Crystalline compounds were prepared by the slow addition of 0.1 *M* aqueous solutions of silver nitrate to ethanolic solutions of the desired heterocyclic amine. The reaction mixture was stirred vigorously during the addition and was then allowed to stand in an ice-bath to facilitate crystallization. The insoluble material was filtered onto a sintered glass filter, washed twice with distilled water, and twice recrystallized from a 50% aqueous alcoholic solution. Purified compounds were dried over calcium chloride and stored *in vacuo* over sulfuric acid.

The silver–amine compounds were analyzed by potentiometric titration in a glacial acetic acid system, using standard perchloric acid as the titrant.[10] A Beckman Model G *p*H meter, equipped with standard glass and saturated calomel electrodes, was used to obtain potential readings. (The calomel electrode was connected to the titration vessel through a sodium perchlorate bridge.) In the titration, both the amine and the nitrate ion are protonated by the titrant. Typical titration curves are shown in Fig. 1.

Absorptimetric Measurements.—Absorptimetric measurements in the ultraviolet region of the spectrum were made on solutions of the amines or on silver–amine compounds with a Cary Model 11 recording spectrophotometer, using 1 cm. matched silica cells. Data in the infrared region of the spectrum were obtained on a double-pass, modified Perkin–Elmer Model 12C spectrometer, equipped with a globar source and a cesium bromide prism, and on a Perkin–Elmer Model 21 spectrophotometer. Spectral grade potassium bromide, a Loomis hydraulic press, a Wig L Bug Amalgamator, and an Evacuable Perkin–Elmer Potassium Bromide Die, 021-0106, were used to prepare pellets of the compounds studied.

Stability Measurements.—Stability constants for the silver–amine compounds in acetonitrile and in ethanol were determined from potentiometric data at 20°. Data were obtained on a Leeds and Northrup Model K 2 potentiometer and a two compartment cell equipped with silver electrodes. Standard silver nitrate solutions, 4×10^{-3} *M*, were used for calibration of the apparatus. The free silver ion concentration in solutions of the silver–amine compounds was ascertained by comparison of the observed potential readings to values on a calibration curve for the particular solvent system.

Determination of Basicity.—Perchlorate salts of 2,2′-bipyridine, 2,2′-biquinoline and 1,10-phenanthroline were prepared by the addition of perchloric acid to an ethanolic solution of the amine, recrystallized from an ether–ethanol mixture, and analyzed by spectrophotometric methods. A Beckman Model G *p*H meter was used to obtain *p*H

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(1) An abstract of a thesis submitted by William J. Peard to the Graduate School of the State University of Iowa, 1957, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) S. M. Jorgensen, *J. prakt. Chem.*, **33**, 501 (1886).

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(5) W. C. Vosburgh and S. A. Cogswell, THIS JOURNAL, **65**, 2412 (1943).

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(8) K. Sone, P. Krumholz and H. Stammreich, *ibid.*, **77**, 777 (1955).

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(10) J. S. Fritz, "Acid–Base Titrations in Nonaqueous Solvents," G. F. Smith Chemical Company, Columbus, Ohio, 1952, pp. 9–23.

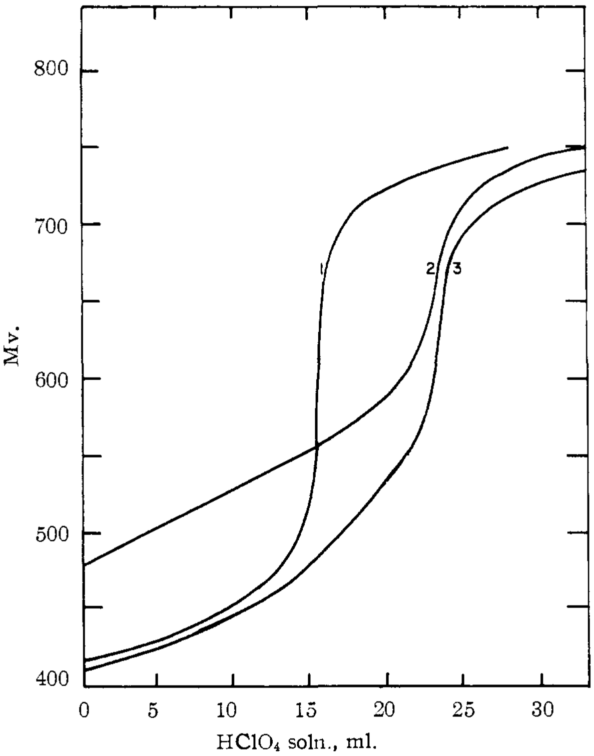

Fig. 1.—Titration curves in glacial acetic acid: Curve (1) 122.5 mg. of pyridine in 100 ml. of acetic acid; (2) 397.0 mg. of silver nitrate in 100 ml. of acetic acid; (3) 259.8 mg. of $Ag(py)_2NO_3$ in 100 ml. of acetic acid.

measurements at 25° on solutions of the salts in a 75% ethanol–water medium.

Results and Discussion

Solid silver–amine compounds, difficultly soluble in water, are generally soluble in alcohol, acetonitrile and in acidic solution. Most compounds were obtained as white or light colored needles. All are stable in air, non-hygroscopic and remain unchanged in color and composition for many months. On heating, most of the compounds melt without decomposition as indicated in Table I.

Certain effects of substitution in the ligands were apparent from observations made during the preparation of the solid compounds. It was found that compounds containing heterocyclic amines with substituent groups in positions adjacent to the nitrogen atom were difficult to prepare. Solid compounds could not be prepared from 2,4-lutidine, 2,4-dimethylquinoline, nor from ligands substituted in the α-position with a hydroxy or halogen group. Inasmuch as 2,6-lutidine readily forms a crystalline compound, a steric consideration cannot be advanced as the controlling factor. Substitution of cyano, halogen, hydroxy or nitro groups into other ring positions does not interfere in the formation of solid compounds.

Analysis of the purified compounds was carried out by potentiometric titrations in glacial acetic acid with perchloric acid as the titrant. Typical titration curves for the silver nitrate–pyridine system are shown in Fig. 1. Data from the titration of pyridine (curve 1) and the nitrate ion (curve 2) permit the simultaneous determination of the two in a titration of $Ag(pyridine)_2NO_3$ (curve 3). The formula of each of the compounds in Table I was determined from similar titrimetric data.

Table I

Descriptive Data on Silver–Heterocyclic Amine Compounds

$Ag(amine)_nNO_3$	n	Description	M.p., °C.
Pyridine	2	White needles	79–84
2-Picoline	2	Slate plates	72
3-Picoline	2	Grey needles	65–75
	3	White needles	87–92
4-Picoline	2	White powder	78
2,6-Lutidine	2	White needles	141–151
2-Cyanopyridine	. .	Yellow needles	. . . . .
4-Cyanopyridine	. .	White needles	. . . . .
Quinoline	2	White needles	106–111
Lepidine	2	Pink powder	142
7-Methylquinoline	2	Pink powder	160
4,8-Dimethylquinoline	1	White needles	150
Isoquinoline	2	White powder	135
3-Methylisoquinoline	2	Pink needles	143
4,7-Dichloroquinoline	. .	Yellow flakes	. . . . .
8-Hydroxyquinoline	. .	Yellow-green powder	. . . . .
6-Methoxylepidine	2	White flakes	65–75
5-Nitroquinoline	. .	White needles	. . . . .
5-Nitroisoquinoline (H_2O)	2	Yellow needles	d 200
4,4′-Bipyridine	1	Tan powder	250
2,2′-Bipyridine	2	Yellow needles	135
2,2′-Biquinoline (H_2O)	2	Green flakes	165–168
1,10-Phenanthroline (H_2O)	2	Green flakes	250

The analysis of the compounds shows that the silver ion is usually bicovalent toward coördinating ligands. Three exceptions were observed. The 3-picoline ligand yields a stable species in which three molecules of amine coördinate with silver. However, the complex is unstable *in vacuo*, losing one mole of amine. The 4,8-dimethylquinoline ligand forms a 1:1 species as does 4,4′-bipyridine. A steric interference may account for the former compound whereas the latter is probably a linear polymer. The 2,2′-bipyridine, 2,2′-biquinoline and 1,10-phenanthroline complexes, although 2:1, reportedly still maintain a linear, bicovalent configuration.[11]

Absorption data in the ultraviolet region of the spectrum were obtained on the heterocyclic amines and on the metal–amine coördination compounds in acetonitrile, chloroform and ethanol. No significant differences were observed in the spectrum of a pure unidentate amine and that of the corresponding metal–amine coördination compound. Small bathochromic shifts in the amine spectrum were found to be characteristic of the bidentate complexes. Marked bathochromic shifts were observed upon the addition of a tenfold excess of silver nitrate to solutions containing these coördination compounds.

The infrared spectra of $Ag(2,2'\text{-bipyridine})_2NO_3$ and 2,2′-bipyridine were obtained in the sodium chloride and in the cesium bromide regions of the spectrum, using potassium bromide pellets con-

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[11] E. Scrocco and M. Ragazzini, *Atti. accad. nazl. Lincei, Rend., Classe sci. fis., mat., e nat.*, **16**, 489 (1954).

taining the compounds in approximately identical concentrations. The intensification of the 7.39 μ band (Fig. 2) is due to the nitrate ion. Figure 3 shows the spectral region in which the absorption spectra of the two compounds differed. (The differences at the higher wave numbers are due to subtraction of water bands from the potassium bromide background and are not to be considered as real deviations.) The spectra indicate that the infrared absorption properties of 2,2′-bipyridine are somewhat modified by coördination with the metal ion.

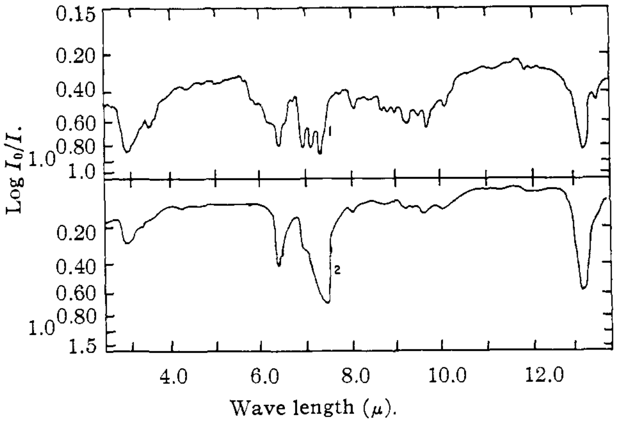

Fig. 2.—Infrared spectra in NaCl region: Curve (1) 5.12 × 10^{-3} mmole of 2,2′-bipyridine/300 mg. KBr; (2) 1.66 × 10^{-3} mmole of $Ag(2,2'\text{-bipy})_2NO_3$/300 mg. KBr.

Results of stability measurements on the 2:1 silver–amine compounds in ethanol and in acetonitrile, computed on the basis of equations 1 and 2, are shown in Table II.

$$Ag(amine)_2^+ \rightleftharpoons Ag^+ + 2amine \tag{1}$$

$$K_S = \frac{[Ag^+][amine]^2}{Ag(amine)_2^+} \tag{2}$$

TABLE II

STABILITY DATA FOR SILVER–AMINE COMPOUNDS

Amine	Amine pK_a	Silver–amine pK_s (ethanol)	Silver–amine pK_s (acetonitrile)
Pyridine	5.17[a]	4.68	4.45
2-Picoline	5.97[a]	5.23	4.99
3-Picoline	5.68[a]	5.05	4.79
4-Picoline	6.02[a]	5.30	5.00
2,6-Lutidine	6.75[a]	5.73	5.47
Quinoline	4.85[c]	4.78	5.12
Lepidine	5.20[b]	5.04	5.48
7-Methylquinoline	5.08[b]	4.86	5.40
Isoquinoline	5.14[c]	4.95	5.27
3-Methylisoquinoline	5.64[d]	5.23	5.71
2,2′-Bipyridine	3.94[e]	8.89	7.00
2,2′-Biquinoline	3.64[e]	10.29	7.55
1,10-Phenanthroline	4.54[e]	13.40	15.04

[a] Values in water at 25°, F. X Mihm, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, pp. 567–662. [b] Values in water at 25°, W. A. Felsing and B. S. Biggs, THIS JOURNAL, **55**, 3624 (1933). [c] Values in water at 20°, A. Albert, R. Goldacre and J. Phillips, *J. Chem. Soc.*, 2240 (1948). [d] Values at 25°, "Dictionary of Organic Compounds," I. Heilbron and H. M. Bunbury, Ed., Eyre and Spottiswoode, London, England, 1953, Vol. III, pp. 449. [e] Values in 75% ethanol-water solutions at 25°.

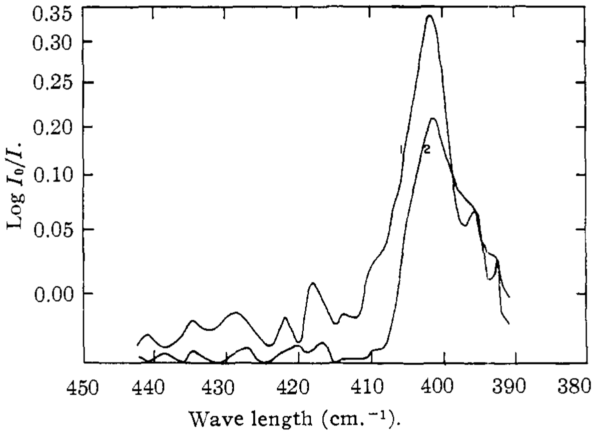

Fig. 3.—Infrared spectra in CsBr region: Curve (1) 5.4 × 10^{-3} mmole of $Ag(2,2'\text{-bipy})_2NO_3$/300 mg. KBr; (2) 1.15 × 10^{-2} mmole of 2,2′-bipyridine/300 mg. KBr.

Values for amine basicity also are tabulated. Plots of pK_s *vs.* pK_a for the pyridine and quinoline type complexes are shown in Fig. 4.

The stability values obtained reflect the competition of the amine ligand and the solvent for the coördination positions of the silver ion. The magnitude of the amine interaction is dependent upon the basicity and structural size of the particular ligand. The solvent–ion interaction is dependent upon the nature and the availability of the dipole of the solvent molecule. Since the over-all stability constant results from a combination of these interactions, it is difficult to interpret the values in terms of any one particular interaction.

Within the same ligand structural type, stability values in any one solvent vary directly with the basic strength of the amine. This is evident from the linear plots for the mononuclear amines, pyridine and methyl-substituted pyridine (curves 1 and 2 on Fig. 4), and for the polynuclear ligands, quinoline and substituted quinolines (curves 3 and 4). Values for the polynuclear bidentate ligands did not follow the order of amine basicity. This might have been expected since a separation of stabilities, on a structural basis, recently has been observed for the zinc complexes of 1,10-phenanthroline and 2,2′-bipyridine in aqueous solution.[12]

Compounds containing mononuclear ligands show maximum stability in ethanol as a solvent. Considering acetonitrile, ethanol and water as solvents and using available stability values for pyridine,[7] 2-picoline[7] and 3-picoline[13] in water, it was found that stability varies inversely as the dielectric constant of the solvent. Plots of pK_s *vs.* the logarithm of the dielectric constant yield a series of straight line not unlike those in Fig. 4.

Coördination compounds of the polynuclear amines are more stable than compounds of the mononuclear ligands. With amines of comparable basicity, stability is increased approximately one *pK* unit in acetonitrile and one-half that amount in ethanol. The bidentate polynuclear amines coördinate very strongly with silver in both sol-

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(13) R. K. Murmann and F. Basolo, THIS JOURNAL, **77**, 3484 (1955).

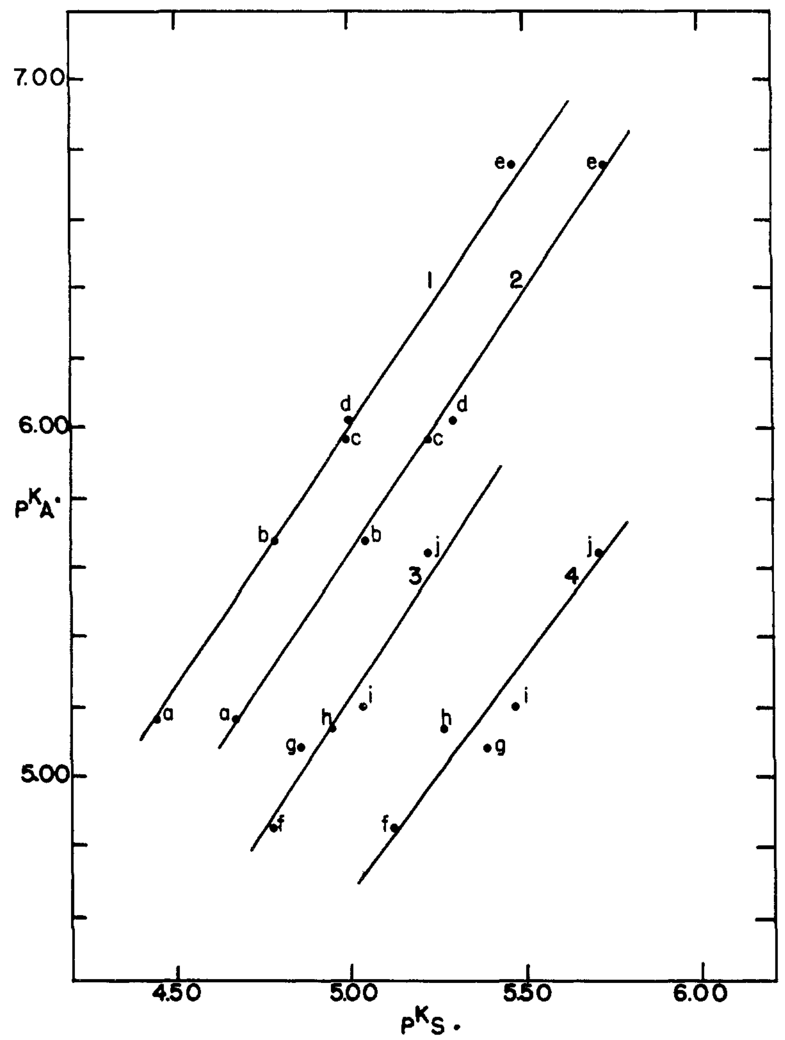

Fig. 4.—Plot of Ag(amine)$_2^+$ stability *vs.* amine basic strength: curve (1) silver–pyridine complexes in acetonitrile; (2) silver–pyridine complexes in ethanol; (3) silver–quinoline complexes in ethanol; (4) silver–quinoline complexes in acetonitrile: a, pyridine; b, 3-picoline; c, 2-picoline; d, 4-picoline; e, 2,6-lutidine; f, quinoline; g, 7-methylquinoline; h, isoquinoline; i, lepidine; j, 3-methylisoquinoline.

vents. The increase in stability results from the increased shielding of the metal ion by the large ligand molecules. With the metal ion insulated from the solvent, the interaction is no longer an ion–dipole interaction between the solvent and the silver ion but rather an interaction between the solvent and the coördinated amine ligands. This accounts for the changes in stability observed in the two solvent systems studied.

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