

The striking increase in the magnitude of the contact shift in passing from the Ni^{+2} to the Co^{+2} complex is obviously due to the presence of unpaired π electrons. Electron delocalization in water complexes must be strongly influenced by π bonding. These results suggest that the Co^{+2} complex should be stabilized by water π donation relative to the Ni^{+2} complex. The anticipated discontinuity between Co^{+2} and Ni^{+2} is, however, not realized in the thermodynamics of metal ion hydration.²⁵ This result gives experimental support for the theoretical prediction of Sugano and Shulman that π

bonding is important in electron delocalization, but σ bonding dominates the bond energy.²⁶

The effect of metal ion charge on the extent of electron delocalization was evaluated for the isoelectronic metal ions Fe^{+3} and Mn^{+2} . The contact shift data indicate that the metal-water bond in the Fe^{+3} complex involves a significantly larger amount of covalency than in the Mn^{+2} complex. This result is consistent with analogous e.s.r. measurements.¹⁶

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(26) S. Sugano and R. G. Shulman, *Phys. Rev.*, **130**, 517 (1963).

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Silver(I) Complexes of Bicyclic Tertiary Amines¹

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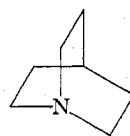
Triethylamine and N,N,N',N' -tetramethylethylenediamine have been compared with their bicyclic analogs, quinuclidine and triethylenediamine, as ligands toward AgNO_3 . Potentiometric titrations in dimethyl sulfoxide, using the cell, $\text{Ag}, \text{AgCl}(\text{satd.}) + \text{NaCl}(\text{satd.}) | \text{NaNO}_3(0.10 M) | \text{NaNO}_3 + \text{AgNO}_3(\mu = 0.1) + \text{amine}, \text{Ag}$ were carried out at 25.0° under N_2 , and the stepwise formation constants were calculated according to Fronaeus. Only 1 mole of triethylamine per $\text{Ag}(\text{I})$ was found to coordinate in DMSO; bis(amine) complexes were formed with the other amines. Solid complexes were prepared, containing (per mole of AgNO_3) 1.5 moles of triethylenediamine or 2 moles of the other amines. The tetramethylethylenediamine complex was characterized as the bis chelate, $[\text{Ag}((\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2]\text{NO}_3$. The complexes of the bicyclic amines with bridgehead nitrogen were more stable thermally with respect to oxidation-reduction than the others; the triethylamine complex decomposed at 0° .

Introduction

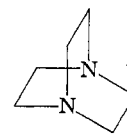
Tertiary aliphatic amines do form metal complexes⁴; however, they are relatively weak ligands. Brown and Sujishi⁵ showed the importance of steric hindrance in a comparison of triethylamine and its bicyclic analog, quinuclidine, as bases toward the reference acid trimethylborane. No comparable study using metal ion reference acids has been reported. A metal cation might show various coordination numbers toward the amine ligands, and competition between amine, anion, and solvent may be expected. Trimethylborane is limited to the formation of 1:1 adducts.

We have studied the silver nitrate complexes of these two amines, and also of two similarly related diamines, N,N,N',N' -tetramethylethylenediamine and its bicyclic analog, triethylenediamine or 1,4-diazabicyclo-

[2.2.2]octane. In addition to differing steric requirements, the latter pair also provide the possible comparison of a chelating and a nonchelating but bidentate diamine.



Quinuclidine



Triethylenediamine

Silver(I) complexes in aqueous or partly aqueous triethylamine-triethylammonium salt systems have been studied previously,⁶ and values have been reported for the first and second complex formation constants. There have been no reports of solid silver(I) triethylamine complexes. No metal complexes of quinuclidine have been reported. Formation of the bis(tetramethylethylenediamine)silver(I) complex ion was demonstrated by Streuli during potentiometric titration of silver(I) perchlorate in anhydrous acetone.⁷ Neither stability studies nor preparations of solid complexes

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(4) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

(5) H. C. Brown and S. Sujishi, *J. Am. Chem. Soc.*, **70**, 2878 (1948).

(6) (a) F. G. Pawelka, *Z. Elektrochem.*, **30**, 180 (1924); (b) H. T. S. Britton and W. G. Williams, *J. Chem. Soc.*, 796 (1935); (c) J. Bjerrum and S. Refn, unpublished results, cited by J. Bjerrum, *Chem. Rev.*, **46**, 387 (1950); (d) C. T. Anderson, Dissertation, The Ohio State University, 1955.

(7) C. A. Streuli, "Titrimetric Methods," D. S. Jackson, Ed., Plenum Press, New York, N. Y., 1961, p. 97.

were reported. Schwarzenbach and co-workers⁸ reported on the 1:1 triethylenediamine silver(I) complex ion in aqueous solution. However, it appears that these workers did not really have the correct amine. The supposed bicyclic diamine was synthesized by the method of Mann and Mukherjee⁹; later work by Mann and Baker¹⁰ indicates that Schwarzenbach, *et al.*, had unfortunately obtained the wrong product.¹¹ Tennenhouse mixed equimolar amounts of silver nitrate and triethylenediamine in dimethylformamide solution and observed precipitation of a material corresponding in composition to a 1:1 complex.¹⁴ It was presumed to be polymeric with bridging triethylenediamine units.

We have studied the stability constants of silver(I) complexes of the four amines in dimethyl sulfoxide (DMSO) and have undertaken the preparation of solid amine-silver(I) nitrate complexes. Similar studies of copper(II) and cobalt(II) complexes of these amines will be reported separately.¹⁵

Experimental Section

Materials.—Triethylamine was purified as described previously.⁴ Quinuclidine was prepared from 4-hydroxyethylpiperidine, kindly supplied by the Reilly Tar and Chemical Corp., according to the method of Leonard and Elkin¹⁸ and purified by vacuum sublimation. Triethylenediamine (trade name Dabco) was kindly supplied by the Houdry Process and Chemical Co. and purified by recrystallization from acetone followed by vacuum sublimation. *N,N,N',N'*-Tetramethylethylenediamine, obtained from the Aldrich Chemical Co., was dried over activated alumina and distilled at reduced pressure. Dimethyl sulfoxide, obtained from the Crown Zellerbach Corp., was purified according to Kolthoff and Reddy.¹⁷ Its water content was shown to be negligible by Karl Fischer titration. Acetonitrile was distilled from phosphorus(V) oxide, shaken three times with cold 50% sodium hydroxide, dried with sodium sulfate, shaken with successive batches of phosphorus(V) oxide until the solid remained dispersed, and distilled under nitrogen, and a middle fraction was collected. Silver nitrate, Mallinckrodt C. P., was heated to fusion and cooled under nitrogen as described by Kolthoff and Sandell.¹⁸

Silver Potentiometry in DMSO.—The cell Ag, AgCl(satd.) + NaCl(satd.)|NaNO₃(0.10 M)|AgNO₃ + NaNO₃($\mu = 0.10$), Ag was used at 25.0°, with DMSO as the solvent throughout the cell. The silver-silver chloride reference electrode has been described by Reddy¹⁹; the solution was prepared by stirring a mixture of dried sodium chloride and silver chloride in DMSO for at least 3 days. The sodium nitrate solution in the salt bridge was contained between two fine-porosity fritted disks in a tube

connecting the electrode chambers. The test solution was stirred with a stream of nitrogen prior to measurement, and a nitrogen atmosphere was maintained in the test electrode chamber. The silver electrodes were made from No. 16 gage wire, 99.5–99.8% pure. A calibrated Leeds and Northrup Model 7401 pH meter was used for potential measurement. Amine-silver(I) complex formation was studied by addition of 10.0 ml. of 0.100 M solutions of the amines, in 0.50-ml. increments, from a buret mounted in a ground-glass joint above the test solution chamber, to 20.0 ml. of (1.00 or 2.50, 5.00, and 10.0) $\times 10^{-3}$ M solutions of silver nitrate in DMSO. Both solutions had been adjusted to ionic strength 0.10 with sodium nitrate.

Conductivity Measurements.—An Industrial Instruments Model 16RC B2 conductivity bridge was used at room temperature. The specific conductance of DMSO was found to range from 2 to 6 $\times 10^{-6}$ ohm⁻¹, but a value of less than 4 $\times 10^{-7}$ ohm⁻¹ was observed when measurements were immediately made after distillation of the DMSO.

Preparation of Solid Complexes.—For work with the two volatile liquid amines, triethylamine and tetramethylethylenediamine, an excess of the amine was condensed on a weighed sample of silver nitrate in a tube attached to a high vacuum line, the mixture was stirred for about 2 days, and the excess of amine was then removed in the course of isothermal pressure-composition measurements of the system. In both the triethylamine system at -16° (equilibrium vapor pressure 8 mm.) and the tetramethylethylenediamine system at 25.0° (equilibrium vapor pressure 16 mm.) the phase diagrams consisted of isobars corresponding to the above vapor pressures at high mole ratios of amine:silver nitrate, falling sharply to negligibly small equilibrium pressures at mole ratios of 2.0. The resulting bis(triethylamine)silver(I) nitrate solid complex was too unstable to permit ready characterization; the corresponding solid tetramethylethylenediamine complex was removed from the reaction tube in a nitrogen-filled drybox and taken for analysis. Mole ratios correspond to the gain in weight of the reaction tube. Silver was determined gravimetrically. *Anal.* Calcd. for AgNO₃·2(C₂H₅)₃N: mole ratio, 2.00. Found: mole ratio, 2.01. Calcd. for AgNO₃·2(CH₂)₂NCH₂CH₂N(CH₂)₂: mole ratio, 2.00; Ag, 26.9. Found: mole ratio, 2.00; Ag, 26.8.

The two solid amines, quinuclidine and triethylenediamine, were sufficiently volatile to permit transfer in a high vacuum line (vapor pressures at room temperature 2 mm. and 1 mm., respectively). To study complexes of these amines with silver nitrate, an excess of the amine in acetonitrile was added to a solution of silver nitrate in acetonitrile in the reaction tube and the mixture was stirred for a 3–7-day period. The acetonitrile was then removed by distillation in the vacuum system. The excess of uncoordinated volatile amine was then removed by pumping in the vacuum system at room temperature. The system was weighed after various time periods and the rate of approach to constant weight was determined. The formulas of the amine-silver nitrate complexes were apparent from the resulting plots of rate of weight loss against composition; moreover, the dissociation pressures of the complexes were negligibly small, so that constant weight corresponded to the stoichiometry of coordination. The products obtained were AgNO₃·2C₇H₁₃N and AgNO₃·1.5C₆H₁₂N₂. Amine content was determined by addition of an excess of standard nitric acid to the sample and potentiometric back titration with standard sodium hydroxide to the first inflection point of the diammonium ion. *Anal.* Calcd. for AgNO₃·2C₇H₁₃N: mole ratio, 2.00; Ag, 27.5; quinuclidine, 56.7. Found: mole ratio, 1.95; Ag, 27.1; quinuclidine, 55.9. Calcd. for AgNO₃·1.5C₆H₁₂N₂: mole ratio, 1.50; Ag, 31.8; triethylenediamine, 49.7. Found: mole ratio, 1.53; Ag, 30.9; triethylenediamine, 49.2. The same triethylenediamine complex was prepared from solution in acetonitrile. A white precipitate formed at once on addition of a solution of 8.23 mmoles of triethylenediamine in acetonitrile to a solution of 4.06 mmoles of silver nitrate in acetonitrile. The mixture was allowed to stand overnight. The precipitate was removed by decantation, washed four times with acetonitrile, and dried at room temperature *in vacuo*. *Anal.*

(8) G. Schwarzenbach, B. Maissen, and H. Ackermann, *Helv. Chim. Acta*, **35**, 2333 (1952).

(9) F. G. Mann and D. P. Mukherjee, *J. Chem. Soc.*, 2298 (1949).

(10) F. G. Mann and F. C. Baker, *ibid.*, 1881 (1957).

(11) In confirmation of this, it may be noted that the pK_a values reported by Schwarzenbach, *et al.*,⁸ do not agree with those determined in the present work for the diprotonated triethylenediammonium ion (3.10 and 8.91 at 25.0° and ionic strength 0.10). Our values agree fairly well with those reported by Parkas, *et al.*,¹² and these sets of data are known to apply to the correct amine since the structure of material from the same source has been determined.¹³

(12) A. Parkas, G. A. Mills, W. E. Erner, and J. B. Maerker, *Ind. Eng. Chem.*, **51**, 1299 (1959); *J. Chem. Eng. Data*, **4**, 334 (1959).

(13) A. S. Parks, Dissertation, University of Pennsylvania, 1963.

(14) G. J. Tennenhouse, Dissertation, University of Illinois, 1963.

(15) J. T. Yoke and H. M. Hilliard, Abstracts, 20th Northwest Regional Meeting of the American Chemical Society, Corvallis, Ore., June 1963.

(16) S. Leonard and S. Elkin, *J. Org. Chem.*, **27**, 4635 (1962).

(17) I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, **108**, 980 (1961).

(18) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Ed., The Macmillan Co., New York, N. Y., 1946, p. 568.

(19) T. B. Reddy, Dissertation, University of Minnesota, 1960.

Calcd. for $\text{AgNO}_3 \cdot 1.5\text{C}_6\text{H}_{12}\text{N}_2$: Ag, 31.8; triethylenediamine, 49.7. Found: Ag, 31.8; triethylenediamine, 49.1.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Infracord, and n.m.r. spectra were obtained with a Varian A-60 n.m.r. spectrometer.

Molecular Weight Determination.—A Model 301A Mechrolab vapor pressure osmometer was used. It was calibrated with chloroform solutions of tetramethylethylenediamine.

Results

The silver electrode in DMSO was found to be reversible and show Nernst law behavior at 25.0° over the 2×10^{-2} to 2×10^{-5} M silver ion concentration range studied. A plot of $p\text{Ag}$ against potential (± 1 mv., vs. the silver-silver chloride reference electrode) was linear with a slope of 60 mv. per log concentration unit and apparent E° (depending on the junction potentials of the particular cell) of 474 mv. Small variations in the concentration of sodium nitrate added had a negligible effect on the potential. These results imply complete dissociation of silver nitrate in DMSO over this concentration range. The equivalent conductance of 10^{-4} M silver nitrate in DMSO was found to be $40 \text{ ohm}^{-1} \text{ cm.}^2 \text{ equiv.}^{-1}$, in excellent agreement with previous values for fully dissociated 1:1 electrolytes, such as sodium nitrate, in DMSO.²⁰

The amine-silver titration data were used to calculate the stepwise complex formation constants by Led- en's method, as modified by Fronaeus. A complete discussion of the method of calculation and of the symbolism used is given by Fronaeus²¹ and by Ahrland, *et al.*²²

In Table I are given the values of the functions used to calculate the formation constants of complexes of silver(I) in DMSO with triethylamine, quinuclidine, and triethylenediamine. The original titration data and graphs accompanying the calculations are given elsewhere.¹ The functions are defined by the equations

$$E_M = (RT/nF) \ln C_{\text{Ag}}/[\text{Ag}^+] = (RT/nF) \ln X$$

$$X = C_{\text{Ag}}/[\text{Ag}^+] = 1 + \beta_1[\text{A}] + \beta_2[\text{A}]^2 + \dots \beta_n[\text{A}]^n$$

$$X_1 = (X - 1)/[\text{A}] = \beta_1 + \beta_2[\text{A}] + \dots \beta_n[\text{A}]^{n-1}$$

$$X_2 = (X_1 - \beta_1)/[\text{A}] = \beta_2 + \beta_3[\text{A}] + \dots \beta_n[\text{A}]^{n-2}$$

where $[\text{A}]$ is the free amine concentration and E_M is the difference between the potential reading at a point in the titration, corresponding to the free silver ion concentration $[\text{Ag}^+]$, and the initial potential reading, corresponding to the total silver ion concentration C_{Ag} . A graphical compensation for dilution during the titration is used. The graphs involved are: first, a plot of E_M vs. total concentration of amine at several values of C_{Ag} , in which lines of constant E_M are drawn to intersect the family of curves obtained; second, a plot of C_{Ag} vs. total concentration of amine at various con-

(20) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(21) S. Fronaeus, "Technique of Inorganic Chemistry," Vol. I, H. B. Jonassen and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, p. 10.

(22) S. Ahrland, J. Chatt, N. T. Davies, and A. A. Williams, *J. Chem. Soc.*, 264 (1958).

TABLE I
FORMATION CONSTANTS FOR COMPLEXES OF TRIETHYLAMINE, QUINUCLIDINE, AND TRIETHYLENEDIAMINE WITH SILVER(I) IN DMSO AT 25.0° AND IONIC STRENGTH 0.10

E_M , mv.	$[\text{A}] (\times 10^3)$	X	$X_1 \times 10^{-2}$	$X_2 \times 10^{-3}$
Triethylamine				
5	5.0	1.215	0.43	...
10	11.8	1.476	0.40	...
15	18.5	1.794	0.43	...
20	26.2	2.180	0.45	...
$X_1 = \beta_1 = K_1 = 4.3 \times 10^1$				
Quinuclidine				
15	5.3	1.794	1.50	5.5
20	7.4	2.180	1.59	5.1
25	9.5	2.649	1.74	5.6
30	12.7	3.218	1.75	4.3
35	15.3	3.910	1.90	4.5
40	17.7	4.751	2.12	5.1
45	20.3	5.773	2.35	5.6
50	24.0	7.015	2.51	5.4
55	27.0	8.523	2.79	5.9
X_1 vs. $[\text{A}]$ intercept $\beta_1 = K_1 = 1.2 \times 10^2$				
$X_2 = \beta_2 = 5.2 \times 10^3$				
$K_2 = \beta_2/K_1 = 4.3 \times 10^1$				
Triethylenediamine				
15	5.2	1.794	1.53	3.6
20	7.2	2.180	1.51	3.6
25	10.3	2.649	1.60	3.9
30	12.8	3.218	1.73	3.9
35	15.8	3.910	1.84	3.3
40	19.8	4.751	1.89	3.7
45	23.0	5.773	2.08	3.7
50	27.0	7.015	2.23	3.7
X_1 vs. $[\text{A}]$ intercept $\beta_1 = K_1 = 1.2 \times 10^2$				
$X_2 = \beta_2 = 3.7 \times 10^3$				
$K_2 = \beta_2/K_1 = 3.0 \times 10^1$				

stant values of E_M , in which the lines obtained are of slope \bar{n} and are extrapolated to zero C_{Ag} to give pairs of corresponding values of $[\text{A}]$ and of E_M (or X); third, a plot of $[\text{A}]$ vs. X_1 , which gives β_1 as intercept; fourth, if necessary, a plot of $[\text{A}]$ vs. X_2 , which gives β_2 as intercept. Further treatment of the data may be undertaken to obtain formation constants of higher complexes, if necessary.

For the tetramethylethylenediamine titrations, values of $[\text{A}]$ at low values of E_M are too small to determine by this method, since the formation constants are much larger. The technique described by Fronaeus²¹ of determining $[\text{A}]$ by graphical integration of a plot of $(1/\bar{n})$ vs. $\log X$ can be used. The required values of \bar{n} are obtained as the slopes of the lines in the second type of graph described above, according to the relation $\bar{n} = (C_{\text{A}} - [\text{A}])/C_{\text{Ag}} = \Delta C_{\text{A}}/\Delta C_{\text{Ag}}$ at constant $[\text{A}]$. In Table II are given the values of the functions used to calculate the formation constants of the tetramethylethylenediamine silver(I) complexes in DMSO.

Values of the equivalent conductance were determined of DMSO solutions 5×10^{-5} to 10^{-3} M in silver nitrate and also 5×10^{-2} to 2×10^{-1} M in tetramethylenediamine; it is apparent from the magnitude of the formation constants in Table II that the predominant metal solute species in these solutions is $[\text{Ag} \cdot 2(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]\text{NO}_3$. The results fell

TABLE II
FORMATION CONSTANTS FOR COMPLEXES OF
TETRAMETHYLETHYLENEDIAMINE WITH SILVER(I) IN DMSO
AT 25.0° AND IONIC STRENGTH 0.10

E_M , mv.	X	\bar{n}	$[A] \times 10^3$	$X_1 \times 10^{-3}$	$X_2 \times 10^{-5}$
30	3.21	0.74	0.800	2.76	10.0
40	4.73	0.96	1.25	2.98	8.0
50	7.00	1.16	1.83	3.28	7.1
60	10.4	1.33	2.40	3.92	7.9
70	15.2	1.42	3.18	4.46	7.9
80	22.4	1.54	4.17	5.13	7.4
90	33.1	1.61	5.25	6.11	7.8
100	49.0	1.67	6.80	7.05	7.5
110	72.5	1.69	8.25	8.66	8.1
120	107	1.68	10.4	10.2	7.9
130	158	1.72	12.4	...	8.6
140	232	2.09	13.7	...	10.9
150	345	1.88	16.8	...	11.0
160	507	1.81	20.7	...	10.8

X_1 vs. $[A]$ intercept $\beta_1 = K_1 = 2.0 \times 10^3$
 $X_2 = \beta_2 = 8.6 \times 10^5$
 $K_2 = \beta_2/K_1 = 4.3 \times 10^2$

in the range 36 to 41 ohm⁻¹ cm.² equiv.⁻¹; such values are typical of completely dissociated 1:1 electrolytes in DMSO.²⁰

The silver nitrate-amine complexes prepared by vacuum line methods were all white solids. Equilibrium was established only very slowly in the triethylamine-silver nitrate system, and there was an indication of formation of an intermediate 1:1 complex in a pressure-composition isotherm at -23°; the rate of interaction was limited by the slow penetration of the solid by the liquid amine, and complex formation was accompanied by a large increase in volume of the solid. The complexes were all stable with respect to dissociation into their components at the temperature of preparation, in that the dissociation pressure in each case was less than 1 mm. Bis(triethylamine)silver(I) nitrate was very unstable with respect to internal oxidation-reduction, however. When the evacuated tube containing the complex was warmed to 0°, the sample melted, giving a silver mirror and a dark liquid. In contrast, bis(quinuclidine)silver(I) nitrate melted with decomposition at 158°, and silver nitrate-1.5-triethylenediamine melted with decomposition at 154-155°.

Bis(N,N,N',N'-tetramethylethylenediamine)silver(I) nitrate showed an intermediate thermal stability; it melted at 100° in a sealed tube under nitrogen, giving a silver mirror and a dark liquid. The proton n.m.r. spectra of the complex and of the free ligand were determined, using separate ca. 20% solutions in deuteriochloroform. Each spectrum consisted of two peaks in the ratio 3:1, corresponding to the four methyl groups and two methylene groups, at 2.52 and 2.59 p.p.m. (vs. tetramethylsilane) for the complex and at 2.22 and 2.38 p.p.m. for the free ligand. A similar but larger shift has been reported between diprotonated tetramethylethylenediamine and the free ligand.²³ The infrared spectrum of the complex both as a Nujol mull and in chloroform solution showed absorptions at 1350 (vs) and 1070 (m) cm.⁻¹ characteristic of the uncoordinated

nitrate ion²⁴; other absorptions characteristic of the nitrate ion at 1460 (s) and 845 (m) cm.⁻¹ were also present, but coincided with bands of the free ligand. Absorptions supposedly characteristic of coordinated nitrate,²⁴ at 1480-1530 and 780-820 cm.⁻¹, were absent. The molecular weight data for the complex (formula weight 402) in chloroform solution were as follows: $9.7 \times 10^{-3} M$, 252; $2.46 \times 10^{-2} M$, 279; $2.97 \times 10^{-2} M$, 284. These values are in accord with an ion-pair dissociation equilibrium $[Ag(\text{amine})_2]NO_3 \rightleftharpoons [Ag(\text{amine})_2]^+ + NO_3^-$, with a dissociation constant of 8.6×10^{-3} . In two runs, a 0.02 M solution of excess amine in chloroform was used as "solvent" in both the test and reference probes of the osmometer; since this did not affect the above equilibrium, it follows that dissociation of coordinated amine is not occurring.

Discussion

All the titration data can be satisfactorily interpreted in terms of formation of only mono- and bis-(amine) silver complexes with quinuclidine, triethylenediamine, and tetramethylethylenediamine, and of only a monoamine complex with triethylamine in DMSO. There is no evidence for the formation of polynuclear complexes in DMSO.

The nonchelating amines form relatively weak complexes. Thus, while K_1 for quinuclidine is significantly larger than K_1 for triethylamine, the difference is a surprisingly small one. A clearer demonstration of the importance of steric hindrance, comparing triethylamine and quinuclidine, is that no significant formation of bis(triethylamine)silver(I) ion is observed in DMSO. Apparently steric interference between two triethylamine molecules coordinated to a silver ion would occur, and in the presence of the solvent DMSO as a competing ligand the bis(triethylamine) complex is not formed. In the absence of solvent, however, the solid bis(triethylamine)silver(I) nitrate does form, though slowly, since the only alternative ligand would be the poorly coordinating nitrate ion.

In DMSO, the formation constants of quinuclidine and triethylenediamine complexes are very similar. Although triethylenediamine has much lower aqueous Brønsted-Lowry basicity¹¹ than does quinuclidine²⁵ (due to the inductive effect of the second nitrogen atom), this difference has nearly disappeared toward silver ion as reference acid in DMSO. A similar compression of the range of base strengths of amines toward silver ion has been noted previously.²⁶

In DMSO solution, triethylenediamine behaves as a monodentate ligand. In solid complexes, however, the formulas and properties of the compounds suggest that it can be a bridging bidentate ligand. The complex $AgNO_3 \cdot C_6H_{12}N_2$, precipitated by Tennenhouse¹⁴ by

(24) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960).

(25) Previous reports of the pK_a of the quinuclidinium ion have not been accompanied by any experimental description of methods or conditions; we observe a pK_a of 11.2 in an aqueous perchlorate medium at 25.0° and ionic strength 0.10 by potentiometric titration.

(26) R. J. Bruhlman and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

mixing equimolar amounts of the components in dimethylformamide, was considered to be a polymer. Tennenhouse and Bailar indicate²⁷ that the 1:1 complex could also be obtained from an equimolar mixture in acetonitrile. However, if in dimethylformamide the mole ratio of amine to silver ion was 3:2 or greater, then they obtained $\text{AgNO}_3 \cdot 1.5\text{C}_6\text{H}_{12}\text{N}_2$, as was observed in the present work using acetonitrile. These products apparently differ in the fraction of diamine which serves as a bridging unit; in neither case has the product been fully characterized nor the structure determined.

With the sterically obstructed tetramethylethylenediamine there is the possibility that the diamine might coordinate to silver ion through only one nitrogen, or that it might act as a chelating agent. The formation constants of the mono- and bis(amine) silver(I) complexes in DMSO are an order of magnitude greater than the formation constants of the complexes of the other amines. In the solid compound $\text{AgNO}_3 \cdot 2(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, three possibilities arise: (1) that each tetramethylethylenediamine is bound through one nitrogen only and that silver is bicoordinate, (2) that the diamine is bidentate and bridges between two silver ions, so that silver is tetracoordinate and the material is a completely cross-linked polymer, (3) that the diamine is chelated and silver is tetracoordinate. Coordination of the nitrate might also be considered. The proton n.m.r. signal suggests that tetramethylethylenediamine is in a symmetrical environment, which is not in accord with the first possibility (unless rapid exchange causes time averaging). The ready solubility of the compound in DMSO and in chloroform observed here, and of the analogous perchlorate in acetone observed by Streuli,⁷ is not in accord with the second possibility (except in the case of a spiro-type linear polymer). Both the formation constants and the other properties do point to chelate formation.

(27) G. J. Tennenhouse and J. C. Bailar, Jr., private communications.

Absence of nitrate coordination is indicated by the infrared data for the solid and for its solution in chloroform, and by the conductance data in DMSO solution; ion-pair association is indicated by the molecular weight measurements in chloroform. It is concluded that the complex is the chelate $[\text{Ag}((\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2]\text{NO}_3$. Since triethylenediamine and tetramethylethylenediamine differ in kind as ligands toward silver(I), no comparison of steric effects between the bicyclic and the open-chain diamine is valid.

This work suggests that nonchelating aliphatic tertiary amines are relatively weak ligands and that reduction of steric hindrance by placing the nitrogen atom at the bridgehead of a bicyclic system has a definite but rather small effect on formation constants, but a more obvious effect on the coordination number of silver ion toward the amine in the presence of competing ligands. High coordination numbers of metal ions toward other bicyclic ligands with bridgehead donor atoms have been reported previously.²⁸

The thermal stabilities of the solid complexes toward oxidation-reduction are not necessarily directly related to the stabilities toward dissociation. In a previous study of internal oxidation-reduction of dichlorobis-(triethylamine)copper(II), a mechanism was postulated involving intermediates with double bonds at nitrogen.²⁹ If oxidation of the amines by silver(I) involved similar structures, then the greater thermal stability of complexes of the bicyclic amines is to be expected according to Bredt's rule against double bonds at a bridgehead.

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(28) For example, J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **2**, 944 (1963).

(29) J. F. Weiss, G. Tollin, and J. T. Yoke, *ibid.*, **3**, 1344 (1964).