Potentiometric Studies on Complexes of Silver(I) in Solutions. Part 2.† Correlation between the Stability of the Silver(I)–Azole Complexes and the Ligand Basicity

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Stability constants of Ag^I complexes with pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole, 1,2,4-triazole, 4-amino-1,2,4-triazole, thiazole, 4-methylthiazole, and 2-aminothiazole have been determined potentiometrically by simultaneous measurement of $[Ag^+]$ and $[H_3O^+]$. All measurements were run at 25 ± 0.1 °C at a ionic strength $I = 0.5$ mol dm^{-3} adjusted with KNO_3. Linear correlations have been found between log β_1, log β_2, and pK_a for these complexes. The contribution of $\pi_{M\to L}$ bonding to the co-ordination bonds is discussed. The π-electron-acceptor strength of unsubstituted azoles has been found to follow the sequence 1,2,4-triazole > pyrazole > thiazole ≫ imidazole.

Silver(I) complexes of pyrazole, 1,2,4-triazole, and thiazole‡ have been investigated in aqueous solution by Blais and Berthon[1] who employed the potentiometric method of measuring the potential of the Ag/Ag^+ electrode. Poddar *et al.*[2] investigated the stability of the Ag^I complexes of pyrazole, 3-methylpyrazole, and 3,5-dimethylpyrazole in aqueous ethanol using the same method.

In a previous paper,[3] a potentiometric method was developed for determining the stability constants of complexes based on simultaneous measurements of the hydrogen and metal ion concentrations at equilibrium. This method was subsequently employed to determine equilibrium constants for complexation of Ag^I with imidazole and methylimidazoles. Continuing the research, we decided to determine the composition and stability of the Ag^I complexes of pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole, 1,2,4-triazole, 4-amino-1,2,4-triazole, thiazole, 4-methylthiazole, and 2-aminothiazole. Complexes of azoles with other transition metal ions have been studied by us previously.[4–7]

An attempt has also been made to correlate the stability of the silver(I) complexes with the basicity of the ligands. Such correlations had been explored by many authors using other ligands.[8,9]

Experimental

Reagents.—Pyrazole (Fluka AG; m.p. 67—69 °C), 3,5-dimethylpyrazole (Aldrich-Europe; m.p. 107—109 °C), 1,2,4-triazole (Merck-Schuchardt; m.p. 119—121 °C), 4-amino-1,2,4-triazole (Merck-Schuchardt; m.p. 80—81 °C), and 2-aminothiazole (Aldrich-Europe; m.p. 91—93 °C) were crystallised twice from doubly distilled water before use. 3-Methylpyrazole (Aldrich-Europe; b.p. 203—205 °C), thiazole (Fluka AG; b.p. 112—115 °C), and 4-methylthiazole (Koch-Light labs. Ltd.; b.p. 131—133 °C) were fractionally distilled before use. The concentrations of the stock solutions of $AgNO_3$, HNO_3, and KNO_3 were determined by conventional methods.

Instrumentation.—The pH measurements were carried out using a PHM-64 (Radiometer, Copenhagen) pH-meter. The e.m.f. was measured with a precision V 540 (Meratronic, Poland) millivoltmeter; G 202 C (glass), K 401 (calomel) (Radiometer, Copenhagen), and silver electrodes (Energopomiar, Poland) were used.

The pH-meter was calibrated against buffer solutions of pH 7.00 and 4.01 (Radiometer, Copenhagen).

Procedure.—The e.m.f. of the concentration cell and the pH of the solution in the measuring cell were determined. A diagram of the measuring assembly is shown in the Scheme. All measurements were run at 25 ± 0.1 °C at a ionic strength $I = 0.5$ mol dm^{-3} adjusted with KNO_3.

Calculations.—The values of Leden's function, F_1, were calculated from equations (1) and (2), where c_{Ag^I} is the

$$\Delta E = \frac{RT}{F} \ln \frac{c_{Ag^I}}{[Ag^+]} \tag{1}$$

$$F_1 = \left(\frac{c_{Ag^I}}{[Ag^+]} - 1\right)\frac{1}{[L]} = \sum_{n=1}^{N} \beta_n [L]^{n-1} \tag{2}$$

analytical concentration of Ag^I ion. The equilibrium ligand concentration, [L], was calculated from equation (3), where K_a

$$[L] = \frac{K_a[HL^+]}{[H_3O^+]} = \frac{K_a(c_a - [H_3O^+])}{[H_3O^+]} \tag{3}$$

is the dissociation constant of the protonated form of the ligand and c_a is the total acid concentration. The stability constants, β_n, were calculated from equation (2) by the least-squares method on an ODRA 1305 computer.

The stability of the thiazole and 4-methylthiazole complexes was independently studied by conventional pH-metry. The equilibrium ligand concentration, [L], and formation function, $\bar{n}$, were calculated from equations (3) and (4) respectively, where

$$\bar{n} = \frac{\sum_{n=1}^{N} n[AgL_n^+]}{c_{Ag^I}} = \frac{c_L - c_a + [H_3O^+] - [L]}{c_{Ag^I}} \tag{4}$$

c_L is the total ligand concentration. The set of the $\bar{n}$ and [L] values was then used to determine the constants β_n using the same program and the Rossotti equation[10] (5). Numerical values of the stability constants are given in Table 1.

$$\frac{\bar{n}}{(1 - \bar{n})[L]} = \beta_1 + \frac{2 - \bar{n}}{1 - \bar{n}}\beta_2[L] \tag{5}$$

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† Part 1 is ref. 3.

‡ Throughout this paper, thiazole refers to 1,3-thiazole.

Table 1. The stability constants of silver(I) complexes with azoles in aqueous solution at 25 °C

Ligand	pK_a	Method[a]	Medium[b]	log ($\beta_1 \pm \sigma$)	log ($\beta_2 \pm \sigma$)
Pyrazole	2.66	Ag, gl	KNO_3 (0.5)	1.88 ± 0.10	4.17 ± 0.008
		Ag[1]	KNO_3 (0.5)	2.11	4.235
		Ag[2]	KNO_3 (0.1)[c]	2.05	4.44
3-Methylpyrazole	3.59	Ag, gl	KNO_3 (0.5)	2.33 ± 0.11	4.94 ± 0.007
		Ag[2]	KNO_3 (0.1)[c]	2.41	4.80
3,5-Dimethylpyrazole	4.10	Ag, gl	KNO_3 (0.5)	2.38 ± 0.05	4.83 ± 0.01
		Ag[2]	KNO_3 (0.1)[c]	3.09	5.54
1,2,4-Triazole	2.50	Ag, gl	KNO_3 (0.5)	2.21 ± 0.11	4.50 ± 0.05
		Ag[1]	KNO_3 (0.5)	2.60	4.38
4-Amino-1,2,4-triazole	2.53	Ag, gl	KNO_3 (0.5)	2.30 ± 0.08	4.43 ± 0.01
Thiazole	2.68	Ag, gl	KNO_3 (0.5)	1.56 ± 0.06	3.73 ± 0.01
		gl	KNO_3 (0.5)	1.42 ± 0.13	3.83 ± 0.3
		Ag[1]	KNO_3 (0.5)	1.95	3.92
4-Methylthiazole	3.13	Ag, gl	KNO_3 (0.5)	1.00 ± 0.10	4.27 ± 0.02
		gl	KNO_3 (0.5)	1.02 ± 0.12	4.42 ± 0.03
2-Aminothiazole	5.57	Ag, gl	KNO_3 (0.5)	2.69 ± 0.05	5.35 ± 0.007
Imidazole	7.18	Ag, gl[3]	KNO_3 (0.5)	3.31 ± 0.04	6.78 ± 0.002
		gl[3]	KNO_3 (0.5)	3.33 ± 0.10	6.96 ± 0.03
1-Methylimidazole	7.19	Ag, gl[3]	KNO_3 (0.5)	2.95 ± 0.10	6.33 ± 0.008
		gl[3]	KNO_3 (0.5)	2.91 ± 0.15	6.56 ± 0.02
2-Methylimidazole	8.05	Ag, gl[3]	KNO_3 (0.5)	3.54 ± 0.15	7.14 ± 0.02
		gl[3]	KNO_3 (0.5)	3.50 ± 0.11	7.25 ± 0.02

[a] Electrodes are stated; gl = glass. [b] Concentrations (mol dm^{-3}) given in parentheses. [c] In 20% aqueous ethanol.

$$(+)\,\mathrm{Ag}\ \Bigg|\ \begin{array}{l}\mathrm{AgNO_3}\ (a)\\ \mathrm{HNO_3}\ (b)\\ \mathrm{KNO_3}\\ (0{\cdot}5-a-b)\end{array}\ \Bigg\|\ \begin{array}{c}\mathrm{KNO_3}\\ (0{\cdot}5)\end{array}\ \Bigg\|\ \begin{array}{c}\mathrm{Ag}\\ (-)\end{array}\ \Bigg|\ \begin{array}{l}\mathrm{AgNO_3}\ (a)\\ \mathrm{HNO_3}\ (b)\\ \mathrm{L}\ (c)\\ \mathrm{KNO_3}\\ (0{\cdot}5-a-b)\end{array}\ \Bigg|\ \begin{array}{c}\mathrm{glass}\\ (+)\end{array}\ \Bigg\|\ \begin{array}{c}\mathrm{KNO_3}\\ (0{\cdot}5)\end{array}\ \Bigg\|\ \begin{array}{c}\mathrm{KNO_3}\\ (0{\cdot}5)\end{array}\ \Bigg|\ \mathrm{KCl_{sat}}\ \Bigg|\ \mathrm{Hg_2Cl_2}\ \Bigg|\ \mathrm{Hg}\ (-)$$

Scheme. Concentrations (mol dm^{-3}) in parentheses: a is a constant over the concentration range 1—3 mmol dm^{-3}; b = 0.05 mol dm^{-3}; c was varied over the range 0—0.15 mol dm^{-3}. L = ligand, sat = saturated

Results and Discussion

Silver(I) *Complexes of Pyrazole,* 1,2,4-*Triazole, Thiazole, and their Derivatives.*—So far, the stability of the silver(I) complexes of azoles has usually been determined by measuring the e.m.f. of a concentration cell.[11-13] The measurements were carried out under conditions in which it was possible to overlook the concentration of the protonated form of the ligand, HL^+, and those of particular AgL_n^+ complexes in equation (6), describing the total ligand concentration.

$$c_L = [L] + \sum_{n=1}^{N} n[AgL_n^+] + [HL^+] \qquad (6)$$

This approach led to correct values if very weak Brønsted bases were used as ligands. When this condition was not satisfied, the pH of solution had to be lowered to avoid formation of hydroxo complexes. It is thus necessary to account for the ligand–proton equilibrium by simultaneous measurement of the pH of solution.[3]

On the basis of the measured values of $[H_3O^+]$ and $[Ag^+]$, the equilibrium ligand concentration, [L], and Leden's function, $F_1 = (c_{Ag^+}/[Ag^+] - 1)/[L]$, were calculated. In all instances the plots of F_1 *vs.* [L] are linear. This means that two mononuclear complexes, AgL^+ and AgL_2^+, exist in each system. Equilibrium constants for these species are listed in Table 1 together with those of the previously studied imidazole complexes.

The stability of the thiazole and 4-methylthiazole complexes was also studied by conventional pH-metry. In Figure 1, the formation curves of the Ag^I complexes with these ligands are shown. The pH-metric method could not have been employed to investigate the complexation of 2-aminothiazole because a precipitate was produced. This difficulty was overcome by simultaneous measurement of the pH and of the potential of the Ag/Ag^+ electrode, as fairly low analytical concentrations of the central ion could be used (lower than those resulting from the solubility product).

Correlation of the Stability of the Complexes with the Ligand Basicity.—Many authors have found linear correlations between the stability of complexes expressed in terms of log β_n or $\frac{1}{n}$ log β_n and the basicity, pK_a, of the ligands.[8,9] These results indicate that the linearity is obeyed exclusively by similar ligands possessing the same electron-donor atom relative to both the metal ion and the proton.

A linear plot of log β_1 *vs.* pK_a, equation (7), with a slope equal

$$\log \beta_1 = a\,\mathrm{p}K_a + b \qquad (7)$$

to unity (a = 1) indicates that the equilibrium constant values

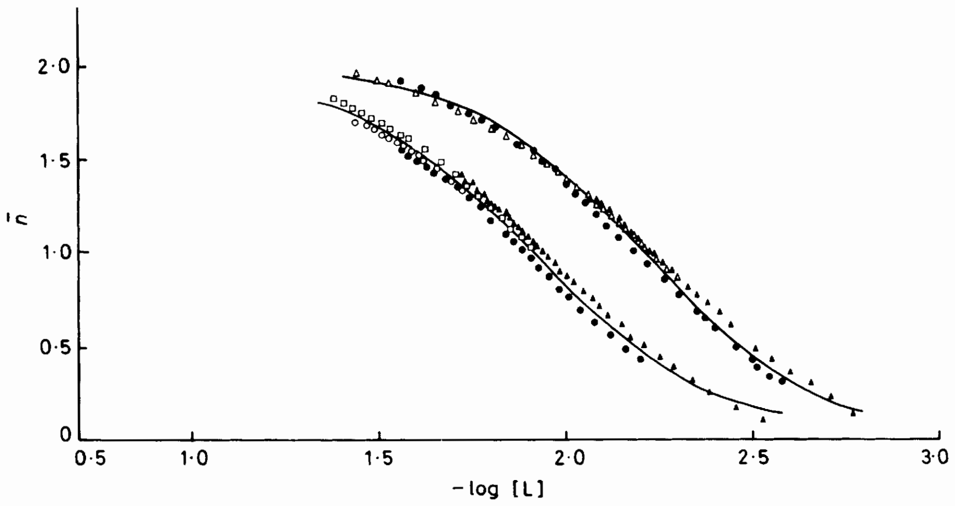

Figure 1. Formation curves of the silver(I) complexes of thiazole and 4-methylthiazole for metal ion concentrations of 20 (○), 30 (□), 50 (●), 60 (△), and 70 mmol dm^{-3} (▲)

Table 2. Values of log *β_1 and $\frac{1}{2}$ log *β_2 for silver(I) complexes with azoles

Ligand	log *β_1	$\frac{1}{2}$ log *β_2
Pyrazole	−0.78	−0.58
3-Methylpyrazole	−1.26	−1.12
3,5-Dimethylpyrazole	−1.72	−1.69
1,2,4-Triazole	−0.29	−0.25
4-Amino-1,2,4-triazole	−0.23	−0.32
Thiazole	−1.12	−0.82
4-Methylthiazole	−2.13	−1.00
2-Aminothiazole	−2.88	−2.90
Imidazole	−3.87	−3.79
1-Methylimidazole	−4.24	−4.03
2-Methylimidazole	−4.51	−4.48

for the reactions of substitution of a proton by a metal ion (8) are identical for all of the ligands considered.

$$M^{m+} + HL^{+} \rightleftharpoons ML^{m+} + H^{+} \qquad (8a)$$

$$\log {}^{*}\beta_1 = \log \frac{[ML^{m+}][H^{+}]}{[M^{m+}][HL^{+}]} = \log \beta_1 - pK_a \qquad (8b)$$

Usually the slopes are smaller than unity, especially with aromatic ligands. The stronger the contribution of the $\pi_{M\rightarrow L}$ bonding to the interaction of a metal ion with a group of similar ligands, the smaller the slope.[9]

A correlation between the stability of the silver(I) complexes with heterocyclic ligands and their basicity has been reported for pyridines,[8,9] the contribution of the $\pi_{M\rightarrow L}$ bonding is obvious in these complexes. There are no reports dealing with the Ag^{I} complexes of azoles.

In Figure 2, log β_1 and log β_2 are plotted *vs.* pK_a for the silver(I) complexes of the azoles. The equations for the linear correlation are as shown, (9a) and (9b).

$$\log \beta_1 = 0.292pK_a + 1.071;\ r_c = 0.841 \qquad (9a)$$

$$\log \beta_2 = 0.514pK_a + 2.835;\ r_c = 0.967 \qquad (9b)$$

The smaller value of the linear regression coefficient, r_c, in equation (9a) is due to a larger error in the determination of the stability constant of the first of the successive formation constants (Table 1). The slopes obtained here are well below unity matching those for the pyridine complexes.[8] This means that the stability of the azole complexes is affected by a massive contribution of the $\pi_{M\rightarrow L}$ bonding to the metal–ligand bonds. The contribution can be estimated from the equilibrium constant, equation (8). The constant determines the stability of the first complex of a ligand with a metal relative to the stability of its proton complexes.[13]

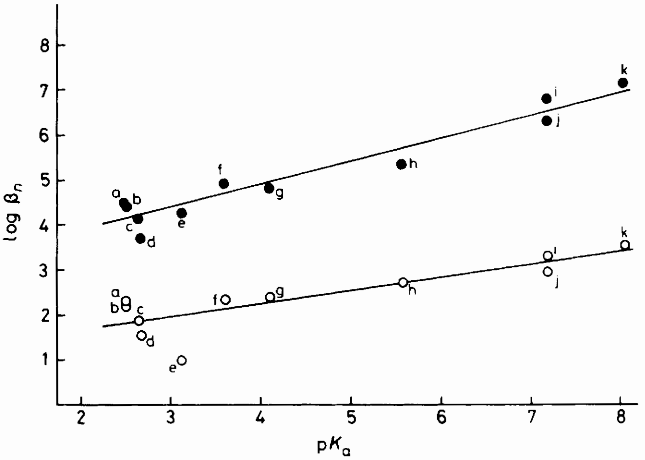

Figure 2. Plots of log β_1 (○) and log β_2 (●) *vs.* pK_a of the ligands for 1,2,4-triazole (a), 4-amino-1,2,4-triazole (b), pyrazole (c), thiazole (d), 4-methylthiazole (e), 3-methylpyrazole (f), 3,5-dimethylpyrazole (g), 2-aminothiazole (h), imidazole (i), 1-methylimidazole (j), and 2-methylimidazole (k)

Numerical values of log *β_1 for the silver(I) complexes are shown in Table 2. Also included there are the $\frac{1}{2}$ log *β_2 values, *β_2 being the equilibrium constant for reaction (10). The data of

$$Ag^{+} + 2HL^{+} \rightleftharpoons AgL_2{}^{+} + 2H^{+} \qquad (10a)$$

$$\log {}^{*}\beta_2 = \log \frac{[AgL_2{}^{+}][H^{+}]^2}{[Ag^{+}][HL^{+}]^2} = \log \beta_2 - 2pK_a \qquad (10b)$$

Table 2 show that the values of both constants are comparable and may provide a starting point for further investigation.

By comparing log $^*\beta_1$ and $\frac{1}{2}$ log $^*\beta_2$ for complexes of a particular metal with various ligands, it is possible to determine variations in the π-electron-acceptor capacity within a group of similar ligands. The data of Table 2 show that the π-electron-acceptor properties of unsubstituted azoles decrease in the order: 1,2,4-triazole > pyrazole > thiazole ≫ imidazole.

In the group of pyrazoles, thiazoles, and imidazoles, the values of log $^*\beta_1$ and $\frac{1}{2}$ log $^*\beta_2$ decrease with increasing ligand basicity. The decrease is due to reduction of the π-electron-donor capacity owing to increase in electron density on the donor nitrogen atom which hinders the transmission of electrons from the metal to the ligand. The log $^*\beta_1$ and $\frac{1}{2}$ log $^*\beta_2$ values are also influenced by steric effects of the substituents situated in the immediate vicinity of the electron donor.

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