

Metal Ammine Formation in Solution

XV. The Silver(I)- and Mercury(II)-Pyridine and Some Other Mercury(II)-Amine Systems

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The experimental data for some of the stability constants given by the author in the first edition of the collection of stability constants³ have never been published. This paper presents those for the silver pyridine and the mercury(II) ammine systems with pyridine, piperidine, methylamine, and butylamine. The stability constants were in all cases obtained from glass electrode measurements at 25°C in 0.5 M solutions of the amine nitrates. The measurements of the silver pyridine solutions gave direct information about the activity decreasing effect of pyridine on the silver pyridine complexes. Further information about the salting-in effect of pyridine was obtained from solubility determinations with dipyridinesilver(I) nitrate. The stability constants were found to be $K_1=10^{2.01}$, $K_2=10^{2.15}$, $\beta_2=10^{4.16}$. The stability constants found for the mercury(II) ammine complexes are given in Table 4. They are only slightly different from those previously published.^{3,4}

An important cause of error when determining the stability constants of the relatively weak pyridine complexes by glass electrode measurements in a more or less constant aqueous salt medium is the strong activity decreasing effect of pyridine on pyridinated ions as well as on the pyridine itself. Owing to this effect one finds too high values for the ligand numbers, which in some cases has led to the postulation of non-existing complexes. This problem was treated in detail in an earlier paper on the copper(II)-pyridine system.¹ Measurements with silver(I)- and mercury(II)-pyridine systems together with some other monoamine systems of these metals were made by the author as early as 1941-45. Stability constants from these studies are published in the literature^{2,3} but the experimental data have never been published. In the meantime many papers have appeared dealing with silver ammine systems but no publications have until now appeared dealing with the mercury(II)-amine systems with pyridine, methylamine, butylamine, and piperidine.⁴ The present author's unpublished data for these systems are treated here together with

a study of the silver pyridine system which also deals with the solubility of dipyridinesilver(I) nitrate. The stability constants were in all cases determined by glass electrode measurements in 0.5 M solutions of the nitric acid salts of the amines at 25°C.

THE SILVER(I)-PYRIDINE SYSTEM

If the stability constants of the silver pyridine complexes are determined at sufficiently low concentrations of pyridine by means of the formula

$$\bar{n} = \frac{C_{\text{py}} + [\text{H}^+] - [\text{py}]}{C_{\text{Ag}}} \quad (1)$$

they are only slightly disturbed by the activity decreasing effect of pyridine. In the more recent literature⁴ there is also rather good agreement between the values for the stability constants K_1 and β_2 obtained by various methods. However, too high values for the ligand number are obtained for pyridine concentrations > 0.05 M. This can be seen from the data collected in Table 1. The calculations were based on the potential differences as measured by glass electrodes between silver(I)-pyridine-0.50 M pyHNO₃ solutions and a standard 0.0485 M pyridine-0.50 M pyHNO₃ solution. What is denoted as the apparent pyridine activity a_{py}' was calculated from the measured potential difference $E - E_{\text{st}}$, according to the expression

$$-\log a'_{\text{py}} = (E - E_{\text{st}})/0.0591 - \log [\text{py}]_{\text{st}} \quad (2)$$

For small pyridine concentrations (solutions 1–6) a_{py}' was identified with [py], and \bar{n} was calculated from formula (1). For higher pyridine concentra-

Table 1. Glass electrode measurements of silver(I)-pyridine solutions in 0.5 M pyHNO₃ at 25°C.

No.	C_{AgNO_3}	C_{py}	$-\log[\text{py}]$	[py]	$[\text{H}^+]$	\bar{n}
1	0.04002	0.00277	2.994	0.00101	0.00303	0.120
2	0.04002	0.00677	2.824	0.00150	0.00205	0.183
3	0.04002	0.01467	2.584	0.00261	0.00118	0.331
4	0.04002	0.02665	2.362	0.00435	0.00071	0.575
5	0.04002	0.03842	2.199	0.00632	0.00049	0.814
6	0.04002	0.05848	1.960	0.01097	0.00028	1.194

Calc. with $-\log [\text{py}] = -\log a_{\text{py}}' - 0.082[\text{py}] - 0.50C_{\text{AgNO}_3}$

No.	C_{AgNO_3}	C_{py}	$-\log a_{\text{py}}'$	a_{py}'	\bar{n}'	$-\log[\text{py}]$	[py]	\bar{n}
7	0.04002	0.0825	1.702	0.01986	1.569	1.680	0.0209	1.540
8	0.0998	0.2056	1.523	0.0300	1.760	1.471	0.0338	1.721
9	0.04002	0.1178	1.371	0.0426	1.882	1.348	0.0449	1.822
10	0.0998	0.2666	1.175	0.0668	2.002	1.119	0.0760	1.910
11	0.1001	0.3101	1.000	0.1000	2.099	0.941	0.1145	1.954
12	0.0998	0.4456	0.685	0.2065	2.396	0.615	0.2428	2.032
13	0.200	0.777	0.555	0.2785	2.493	0.424	0.377	2.000
14	0.0998	0.5932	0.484	0.328	2.657	0.402	0.396	1.976
15	0.0998	0.7895	0.327	0.471	3.319	0.229	0.590	1.999

tions (solutions 7–15) the ligand numbers obtained by using this approximation denoted \bar{n}' , and the corrected ligand numbers calculated by means of the relationship

$$-\log[\text{py}] = -\log a_{\text{py}}' + \log F \quad (3)$$

in which $\log F$ is given by the expression:

$$\log F = -0.082[\text{py}] + \alpha C_{\text{Ag}} \quad (4)$$

According to previous experimental results¹ the coefficient α must be assumed to have a weak positive value for the aqua silver ion and negative values for the pyridine complexes increasing with the number of pyridine ligands taken up. In order to calculate α some assumption must be made. Considering what is known about silver(I)-amine formation in aqueous solution,^{4,6} the complex formation with pyridine must come to a stop when two pyridine ligands are taken up, and under this assumption an average value of α for the solutions in question with $\bar{n} > 1.5$ is determined by trial and error to be -0.50 . The uncorrected points (\bar{n}' , $-\log a_{\text{py}}'$) as well as the corrected points calculated with $\alpha = -0.50$ (\bar{n} , $-\log[\text{py}]$) are plotted in Fig. 1, and

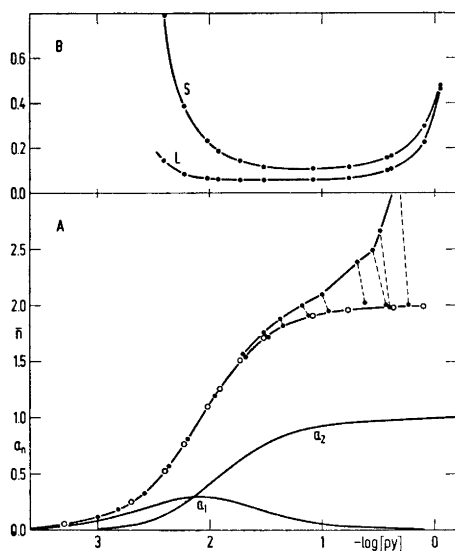


Fig. 1. The silver(I)-pyridine system. Division A gives the formation curve (\bar{n} versus $-\log[\text{py}]$) in 0.5 M pyHNO_3 at 25°C. Stippled lines are drawn between the uncorrected (\bar{n}' , $-\log a_{\text{py}}'$) and the corrected (\bar{n} , $-\log[\text{py}]$) experimental points. The \circ points which closely follow the corrected experimental points are calculated with $K_1 = 10^{2.01}$, and $\beta_2 = 10^{4.16}$. Calculated curves for the degrees of formation of the mono- and dipyridine complexes α_1 and α_2 , respectively, are also given in the figure. Division B. The s -curve gives the solubility of $\text{Ag py}_2\text{NO}_3, \text{aq}$ ($s = C_{\text{Ag}}$), and the L -curve the solubility product $L = \alpha_2 s(s + 0.5)$ as function of $-\log[\text{py}]$ in 0.5 M pyHNO_3 at 25°C.

the figure shows graphically how much the correction influences the last part of the formation curve. The values for the stability constants of the silver pyridine complexes in 0.5 M pyHNO_3 at 25°C:

$$K_1 = 10^{2.01}, K_2 = 10^{2.15}, \beta_2 = 10^{4.16}$$

given by J. Bjerrum in the literature,^{2,3} are average values calculated from the first part of the formation curve (solutions 1–6) with an uncertainty of about $10^{0.02}$. The \circ points which closely follow the corrected formation curve were

calculated by means of these constants. The degrees of formation of the mono- and dipyridine complexes α_1 and α_2 , respectively, were also calculated and the curves are given for comparison. The data are in all cases plotted *versus* $-\log[\text{py}]$, and are supposed to be valid for 0.5 M pyHNO_3 with $C_{\text{Ag}} \sim 0$. For the higher concentrations of pyridine an activity correction was introduced by using the apparent pyridine activity $a_{\text{py}}' = [\text{py}] \times 10^{-0.082[\text{py}]}$ instead of $[\text{py}]$ in the mass action calculations. Another possibility was to introduce a_{py} , which is known from pyridine tension measurements,¹ but a_{py}' is probably a better choice as this function also to some extent corrects for the change in the activity coefficients of the complexes caused by the presence of the pyridine.

Silver nitrate is very soluble in waterfree pyridine. According to the literature,⁵ a solid $\text{AgNO}_3 \cdot 2\text{py}$ corresponding to the complex ion Ag py_2^+ is in equilibrium with the saturated solution above 48°C, between 48°C and -25°C the solid has the composition $\text{AgNO}_3 \cdot 3\text{py}$, and below -25°C finally the compound $\text{AgNO}_3 \cdot 6\text{py}$ is the stable solid. In aqueous pyridine solutions the solid in equilibrium with the saturated solution is the dipyridine compound with 3 to 4 mol of crystal water. The water molecules are lost when the salt is dried and most likely they correspond to the additional pyridine molecules in $\text{AgNO}_3 \cdot 3\text{py}$ and $\text{AgNO}_3 \cdot 6\text{py}$. The solubility of the compound $\text{AgNO}_3 \cdot 2\text{py} \cdot \text{aq}$ was studied in 0.5 M pyHNO_3 at 25°C (for details, see experimental part), and the solubility curve $s = C_{\text{Ag}}$ *versus* $-\log[\text{py}]$ is given in Fig. 1B. The curve for the dependence of the solubility product

$$L = \alpha_2 s(s + 0.5) \text{ mol}^2/\text{liter}^2$$

is also calculated and given in Fig. 1B. As would be expected, the solubility product is more constant than the solubility s , but it will be seen that also L increases for large as well as for small values of $-\log[\text{py}]$. In case of small concentrations of free pyridine the solubility must necessarily increase because of the small degrees of formation of Ag py_2^+ , and when also L increases with decreasing concentration of free pyridine, it must be considered that not only the salt concentration but also the total pyridine concentration increases. In case of high concentrations of pyridine all silver is found as Ag py_2^+ , and the strong increase in the solubility product demonstrates very distinctly the strong activity decreasing effect of pyridine on the silver pyridine complex.

THE MERCURY(II)-AMINE SYSTEMS

As shown by J. Bjerrum,⁶ the mercury(II) ion takes up two ammonia molecules even in acid ammonium salt solutions to form a very stable diammine complex which first at much higher ammonia concentrations is converted into a tetrammine complex. Data for the formation of the bis(amine) mercury(II) complexes with mono-, di-, and triethanolamine have later been published by Bjerrum and Refn.⁷ In the present paper these data are extended with measurements of the mercury(II) complex formation with pyridine, piperidine, methylamine and butylamine. Glass electrode measurements were made of solutions to which stoichiometrical concentrations of mercury(II)

nitrate ($C_{\text{Hg}(\text{NO}_3)_2}$), nitric acid (C_{HNO_3}), amine (C_{am}) and amine nitrate (C_{amHNO_3}) were added. As pure metalamine formation can be assumed,⁶ the average number of bound amine molecules per mercury ion is given by the general formula:

$$\bar{n} = \frac{C_{\text{am}} - C_{\text{HNO}_3} + [\text{H}^+] - [\text{am}] - [\text{OH}^-]}{C_{\text{Hg}}}, \quad (5)$$

where the hydroxyl ion concentrations are negligible in all the cases examined here. The actual hydrogen ion concentration $[\text{H}^+]$ was determined from the formula

$$\text{pH} = -\log [\text{H}^+] = \frac{E_{\text{st}} - E}{0.0591} + \text{pH}_{\text{st}} \quad (6)$$

Table 2. Glass electrode measurements of acid mercury(II)-amine solutions at 25°C.

Pyridine: $C_{\text{pyHNO}_3} = 0.500 \text{ M}$							
No.	$C_{\text{Hg}(\text{NO}_3)_2}$	C_{HNO_3}	C_{am}	$-\log[\text{H}^+]$	$[\text{amH}^+]$	$-\log[\text{am}]$	\bar{n}
1	0.0375	0.1252	0	0.759	0.450	4.80	1.31
2	0.0400	0.1190	0	0.763	0.442	4.80	1.34
3	0.0399	0.1187	0.0595	0.920	0.498	4.59	1.43
4	0.0376	0.1256	0.0803	0.971	0.519	4.52	1.64
5	0.0376	0.1256	0.0990	1.052	0.537	4.43	1.65
6	0.0400	0.1190	0.1193	1.156	0.545	4.32	1.75
7	0.0399	0.1187	0.1495	1.364	0.572	4.09	1.85
8	0.0376	0.1256	0.1695	1.557	0.598	3.88	1.90
Piperidine: $C_{\text{pipHNO}_3} = 0.400 \text{ M}$, $C_{\text{KNO}_3} = 0.100 \text{ M}$							
No.	$C_{\text{Hg}(\text{NO}_3)_2}$	C_{HNO_3}	C_{am}	$-\log[\text{H}^+]$	$[\text{amH}^+]$	$-\log[\text{am}]$	\bar{n}
1	0.00996	0.00991	0.01072	2.378	0.406	9.134	0.502
2	0.01013	0.01007	0.01658	2.684	0.408	8.825	0.847
3	0.01000	0.00995	0.02007	2.887	0.408	8.622	1.142
4	0.01022	0.01016	0.02464	3.121	0.409	8.387	1.491
5	0.01021	0.01015	0.02828	3.520	0.410	7.987	1.805
Methylamine: $C_{\text{meHNO}_3} = 0.497 \text{ M}$ (Nos. 1–3, 5), 0.500 M (Nos. 4, 6)							
No.	$C_{\text{Hg}(\text{NO}_3)_2}$	C_{HNO_3}	C_{am}	$-\log[\text{H}^+]$	$[\text{amH}^+]$	$-\log[\text{am}]$	\bar{n}
1	0.01975	0.02021	0	1.726	0.488	9.305	0.434
2	0.01975	0.00026	0	1.886	0.484	9.148	0.645
3	0.01975	0.00026	0.01106	2.084	0.489	8.945	0.964
4	0.02568	0	0.02606	2.209	0.494	8.816	1.255
5	0.01975	0.00026	0.02975	2.517	0.494	8.508	1.647
6	0.02564	0	0.04229	2.618	0.498	8.404	1.743
Butylamine: $C_{\text{buHNO}_3} = 0.500 \text{ M}$							
No.	$C_{\text{Hg}(\text{NO}_3)_2}$	C_{HNO_3}	C_{am}	$-\log[\text{H}^+]$	$[\text{amH}^+]$	$-\log[\text{am}]$	\bar{n}
1	0.01981	0.01994	0	1.552	0.492	9.466	0.409
2	0.01878	0.01264	0	1.646	0.490	9.374	0.530
3	0.01981	0.00004	0	1.834	0.485	9.190	0.738
4	0.01981	0.00004	0.01016	1.969	0.489	9.052	1.053
5	0.01981	0.00004	0.02167	2.187	0.494	8.829	1.420
6	0.01981	0.00004	0.02831	2.369	0.496	8.645	1.644
7	0.01981	0.00004	0.03475	2.689	0.498	8.324	1.856

Table 3. Glass electrode measurements of basic mercury(II)-amine solutions at 25°C.
 Pyridine: $-\log[\text{py}] = -\log a_{\text{py}}' - 0.082[\text{py}] - 0.50C_{\text{Hg}}$

No.	C_{amHNO_3}	$C_{\text{Hg}(\text{NO}_3)_2}$	C_{am}	$-\log[\text{am}]$	$[\text{am}]$	$[\text{H}^+]$	\bar{n}
1	0.626	0.0376	0.0856	1.989	0.00102	0.00039	2.02
2	0.626	0.0376	0.1080	1.524	0.0299	0.00013	2.08
3	0.626	0.0376	0.1434	1.199	0.0632	0.00006	2.13
4	0.626	0.0376	0.1789	1.025	0.0944	0.00004	2.22
5	0.626	0.0500	0.2771	0.800	0.1585	0.00002	2.37
Methylamine							
1	0.500	0.0399	0.0994	1.753	0.0177	5.4×10^{-10}	2.05
2	0.500	0.0398	0.2067	0.936	0.1159	8.3×10^{-11}	2.28
3	0.500	0.0399	0.2517	0.814	0.1535	6.2×10^{-11}	2.46
4	0.500	0.0399	0.3049	0.681	0.2085	4.6×10^{-11}	2.42
Butylamine							
1	0.500	0.01981	0.05242	1.970	0.01072	9.3×10^{-10}	2.10
2	0.500	0.01981	0.06887	1.596	0.02535	3.9×10^{-10}	2.20
3	0.500	0.01981	0.08146	1.442	0.03614	2.8×10^{-10}	2.29
4	0.500	0.01981	0.08913	1.385	0.0412	2.4×10^{-10}	2.42
5	0.500	0.01981	0.1013	1.288	0.0515	1.9×10^{-10}	2.51
6	0.500	0.06944	0.2537	1.179	0.0662	1.5×10^{-10}	2.70

where pH_{st} and E_{st} refer to a standard acid solution having analogous composition and ion concentration. In case of more strongly acid solutions ($\text{pH} < 2$), pH_{st} was chosen by the method of trial and error to deviate only a few tenths of a pH unit from the pH of the complex solution. The actual ammonium ion concentration is given by

$$[\text{amH}^+] = C_{\text{amHNO}_3} + C_{\text{HNO}_3} - [\text{H}^+] \quad (7)$$

The concentration of free amine is calculated from the knowledge of $[\text{amH}^+]$, $[\text{H}^+]$, and the $\text{p}K_{\text{a}}$ of the amine. Values of $\text{p}K_{\text{a}}$ for pyridine (5.21), piperidine (11.12), methylamine (10.70), and butylamine (10.72) are known from earlier determinations^{1,3,8} under the conditions used here (see Table 2).

The experimental data are given in Tables 2 and 3. It was only necessary to use the more general formulae (5) and (7) in case of the acid solutions of mercuric complexes (Table 2). For the basic solutions of mercuric complexes (Table 3) the conditions are simpler as only C_{am} contributes to the complex formation, and $[\text{amH}^+] = C_{\text{amHNO}_3}$. The concentration of free amine or more correctly a_{am}' could, therefore, be calculated directly from the potential difference towards a standard amine solution with the same ammonium concentration as the complex amine solution. For the aliphatic amines a_{am}' deviates only little from $[\text{am}]$ in the range of concentrations used here (see Table 3). Some measurements with butylamine showed that the salt effect is at least four times smaller than found for pyridine. A correction was, therefore, only introduced in case of the pyridine system, assuming the activity decreasing coefficient to have the same value ($\alpha = -0.50$) as found in the silver pyridine system. The corrected values only are given in Table 3. Fig. 2 gives the formation curves (\bar{n} versus $-\log[\text{am}]$) for all the Hg(II)-amines studied. In the

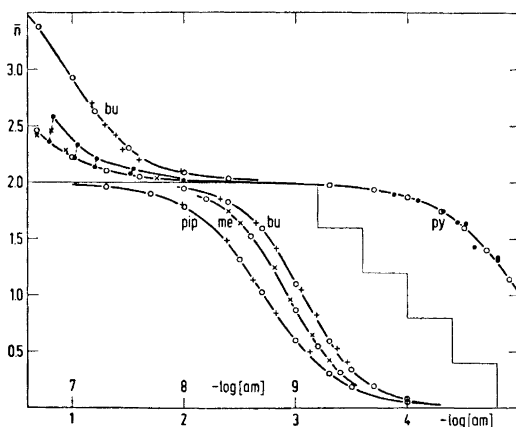


Fig. 2. Formation curves (\bar{n} versus $-\log[\text{am}]$) for the mercury(II)-amine systems in 0.5 M amHNO₃ at 25°C. Note that the figure has two divisions for $-\log[\text{am}] < 5$ and > 7 . The experimental points have the signature ● for pyridine (py), × for methylamine (me), + for butylamine (bu) and piperidine (pip). For the pyridine system at high concentrations ($\bar{n} > 2$) the uncorrected as well as the corrected formation curve are given. The ○ points through which the curves are drawn are calculated by means of the stability constants given in Table 4.

pyridine system is also shown the uncorrected formation curve (\bar{n}' versus $-\log a_{\text{py}}'$). The ○ points are calculated by means of the stability constants, and it will be seen how well the curves drawn through these points agree with the experimental points. The stability constants given in Table 4 are with small changes the same as the prepublished values.³ In Table 4 they are compared with the constants in the Hg(II)-ammonia system (in 2 M NH₄NO₃ at 22°C).⁶ The methylamine, butylamine, and piperidine behave very much like ammonia. The consecutive constants for taking up the two first amine molecules are all of the same order of magnitude $\sim 10^9$ showing that also for piperidine^{2,6} steric factors are of only minor importance. It is also characteristic that the bis(amine) complexes after a long stability range show the same tendency as ammonia (piperidine was not studied in this concentration range) to take up two more amine molecules. The two first pyridine constants are also about equal in size, but much smaller than for ammonia and the aliphatic amines in accordance with a general rule.² The measurements give further strong evidence for the formation of a tetrapyridine complex at high pyridine concentrations.

Table 4. Stability constants of Hg(II)-amine complexes in ~ 0.5 M amHNO₃ at 25°C.

	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_3$	$\log K_4$	$\log \beta_4$
Ammonia	8.8	8.7	17.5	1.00	0.78	19.3
Methylamine	8.66	9.2	17.86	(0.3)	(0.3)	18.5
Butylamine	8.74	9.4	18.14	0.9	1.0	20.0
Piperidine	8.74	8.7	17.44			
Pyridine	5.1	4.9	10.0	0.3	0.3	10.6

EXPERIMENTAL

Chemicals. All reagents were *pro analysi* or of good commercial quality. Of the amines used, the pyridine and butylamine were distilled and analyzed as previously described.^{1,8} The aqueous methylamine was a Kahlbaum product, and the piperidine (Riedel-de Haën) was purified for traces of pyridine by extracting the partly neutralized aqueous amine solution with benzene.

Solutions. The various solutions were prepared in calibrated measuring flasks by weighing or pipetting from stock solutions. The stock solutions of mercury(II) nitrate were prepared from mercury(II) oxide and titrated nitric acid in excess. Stock solutions of the amine nitrates were prepared by careful neutralization of the amines with 5 M nitric acid. The equivalence of acid and base in the solutions was determined by pH-measurements, and a correction was also made when necessary for the self-dissociation of the protonated amine.

Glass electrode measurements. These measurements were made as previously described⁷ with a Radiometer potentiometer, PH M3. The glass electrodes were especially selected and proved to have theoretical pH-dependence even in solutions with pH close to 10. The whole set-up was placed in an air thermostat at $25 \pm 0.1^\circ\text{C}$.

Solubility measurements. The solubility curve for $\text{Ag py}_2\text{NO}_3, \text{aq}$ was determined as follows: Weakly supersaturated solutions were made from silver nitrate and pyridine in 0.5 M pyHNO_3 . After equilibration in a thermostat at 25°C , the solution as well as the precipitate were analyzed. The precipitate analyzed in all cases as dipyridine silver(I) nitrate with 3 to 4 weakly bound water molecules. The results of the solubility measurements are given in Table 5. The initial concentrations of silver nitrate and pyridine are

Table 5. Solubility of $\text{Ag py}_2\text{NO}_3, \text{aq}$ at varying pyridine concentration in 0.5 M pyHNO_3 at 25°C .

No.	C_{Ag}°	C_{py}°	$C_{\text{Ag}} (=s)$	$C_{\text{py}}(\text{calc})$	$C_{\text{py}}(\text{exp})$	[py]	\bar{n}	α_2	L
1	0.843	0.517	0.797	0.425	—	0.0040	0.53	0.140	0.145
2	0.398	0.3235	0.388	0.3035	0.302	0.0059	0.77	0.240	0.083
3	0.2502	0.3000	0.2323	0.2642	0.262	0.0096	1.10	0.402	0.068
4	0.2000	0.2747	0.1863	0.2473	—	0.0123	1.26	0.490	0.063
5	0.1508	0.2490	0.1434	0.2342	—	0.0186	1.50	0.632	0.058
6	0.1992	0.395	0.1157	0.228	—	0.0305	1.71	0.769	0.055
7	0.1197	0.3128	0.1048	0.283	0.283	0.084	1.90	0.913	0.058
8	0.1508	0.4688	0.1144	0.396	0.398	0.172	1.95	0.957	0.067
9	0.2021	0.7779	0.1557	0.685	0.693	0.378	1.980	0.980	0.100
10	0.259	0.928	0.1657	0.741	—	0.414	1.982	0.982	0.107
11	0.3015	1.406	0.2868	1.377	1.370	0.807	1.990	0.990	0.224
12	0.675	2.479	0.478	2.09	2.16	1.14	1.992	0.992	0.464

denoted C_{Ag}° and C_{py}° . The solubilities $s = C_{\text{Ag}}$ were determined by Volhard titrations, and the pyridine concentrations in the saturated solutions were calculated from the initial concentrations:

$$C_{\text{py}}(\text{calc}) = C_{\text{py}}^\circ - 2(C_{\text{Ag}}^\circ - s)$$

Total pyridine nitrogen determinations

$$C(\text{total N}) = C_{\text{py}}(\text{exp}) + 0.500$$

were in some cases made as a control. For this purpose a modified Kjeldahl analysis worked out for heterocyclic nitrogen was used.⁹ The ligand numbers and the concentrations of free pyridine were approximated by means of the \bar{n} , $-\log[\text{py}]$ formation curve valid for 0.5 M pyHNO_3 and the relationship $\bar{n}s = C_{\text{py}} - [\text{py}]$. The final calculations of these quantities, and α_2 and the solubility product $L = \alpha_2 s(s + 0.5)$ were performed using $\alpha_{\text{py}}' = [\text{py}] \times 10^{-0.082[\text{py}]}$ instead of $[\text{py}]$ in the mass action calculations.

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