

Metal Ammine Formation in Solution

XVI. Stability Constants of Some Metal(II)-Pyridine System

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In the Tables of Stability Constants^{1,2} the author has presented values for the stability constants for pyridine complexes of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and Cd^{2+} , the measurements of which have not been published. This paper gives the experimental data, and a discussion of the slightly revised constants (see Table 2).

Metal pyridine complex formation was studied by glass electrode measurements by the author (as early as in 1941-45) partly in cooperation with Else Plejl. The data were used in a review article,³ and our values for the pyridine stability constants of nine metal ions are presented in Tables of Stability Constants.^{1,2} However, only the measurements with Cu^{2+} , Ag^+ , and Hg^{2+} are published in detail.^{4,5} As pointed out in these publications, an important cause of error appears when determining the stability constants of the relatively weak pyridine complexes by glass electrode measurements, an error caused by "the strong activity decreasing effect of pyridine on pyridinated ions as well as on the pyridine itself". Probably owing to this effect, some authors have found too high values for the stability constants, especially at high pyridine concentrations. Thus Atkinson and Bauman⁶ by glass electrode measurements determine $\log K_1$ in the Mn(II)-system to be as high as 1.86 compared to the author's value 0.14 (see Table 2). Owing to this and other disagreements with data in the newer literature, the author has found it appropriate to contribute to the discussion by publishing in detail also the remaining part of the old measurements. The stability constants were in all cases determined by glass electrode measurements at 25°C in 0.5 M pyridinium nitrate solutions with varying concentrations of metal(II) salt and pyridine.

EXPERIMENTAL

Solutions. The various solutions were prepared in calibrated measuring flasks by weighing or pipetting from stock solutions of metal(II) salt, pyridinium nitrate, and pyridine.

The stock solutions of manganese(II) and iron(II) were the chlorides, in all other cases the nitrates. Good quality chemicals were used, and the solutions were analyzed by conventional methods. The stock solutions of the metal(II) salts were stabilized with a small titrated excess of acid. This was especially necessary for the iron(II) chloride solution, which was prepared under air-free condition, and found to contain less than 0.5 % iron(III).

The pyridine was distilled and analyzed as previously described.⁴ A 2.5 M stock solution of pyridinium nitrate was prepared by neutralizing pyridine with 5 M nitric acid. The small excess of acid or base in the pyridinium nitrate stock solution was determined by pH-measurements.⁴

The iron(II)-, manganese(II)-, and cobalt(II)-pyridine solutions were prepared under airfree conditions, and oxidation during the measurements was found to be negligible.

Glass electrode measurements. These measurements were made as previously described.⁷ A Radiometer potentiometer, PHM3, was used. The glass electrodes were especially selected and proved to have a theoretical pH-dependence. The whole apparatus was placed in an air thermostat at $25 \pm 0.1^\circ\text{C}$.

TREATMENT OF MEASUREMENTS

The data for all the metal ions studied are collected in Table 1. The calculations were based on the potential differences, as measured by glass electrodes, between the metal(II)-pyridine-0.5 M pyHNO₃ solution and a standard 0.5 M pyHNO₃ solution with a small known pyridine concentration in the range 0.02–0.04 M. 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

$$-\log a_{\text{py}}' = (E - E_{\text{st}})/0.0591 - \log [\text{py}]_{\text{st}} \quad (1)$$

As discussed in the preceding papers,^{4,5} the relationship between the pyridine concentration and a_{py}' is given by the expression

$$-\log [\text{py}] = -\log a_{\text{py}}' - 0.082[\text{py}] + \alpha C_{\text{M}} \quad (2)$$

The experimental factor 0.082 corrects for the influence of the pyridine itself, and α is a salting-out factor found to have weak positive values for aqua ions and negative values for the pyridine complexes and increasing with the number of pyridine ligands taken up. Utilizing this knowledge, the following relationship has been assumed to be valid

$$\alpha = \frac{1}{2}(0.5 - \bar{n}) \quad (3)$$

The expression is made to agree with what has been found for the Cu(II) system in 0.5 M pyHNO₃, $\alpha \sim -0.4$ for $\bar{n} \sim 3.5$,⁴ and gives a correction for the weakly salting-out effect of the aqua metal ions by estimating that $\alpha \sim 0$, when half of the aqua ions have been converted into monopyridine complex. Utilizing the expressions (2) and (3),

$$\bar{n}_{\text{exp}} = \frac{C_{\text{py}} + [\text{H}^+] - [\text{py}]}{C_{\text{M}}} \quad (4)$$

is calculated from the experimental data and given in Table 1. In expression (4), for the average ligand number, C_{py} and C_{M} are the stoichiometrical concentrations of pyridine and metal(II) salt. The stoichiometrical pyridine con-

Table 1. Glass electrode measurements in metal(II) nitrate solutions in 0.5 M pyHNO₃ at 25°C.

$$-\log[py] = -\log a'_{py} - 0.082[py] - \frac{1}{7}(\bar{n} - 0.5)C_M$$

Mn(II): logK₁ 0.14, logβ₂ -0.4

No.	C _M	C _{py}	-log a' _{py}	\bar{n}'	-log[py]	[py]	[H ⁺]	$\bar{n}_{exp.}$	$\bar{n}_{calc.}$
1	0.0963	0.1002	1.045	0.104	1.043	0.0906	0.00003	0.098	0.114
2	0.2044	0.2351	0.733	0.246	0.7255	0.1882	-	0.229	0.223
3	0.3108	0.3491	0.599	0.313	0.587	0.2588	-	0.290	0.284
4	0.3445	0.5086	0.447	0.440	0.422	0.3782	-	0.379	0.382

Fe(II): logK₁ 0.6, logβ₂ 0.9

1	0.04125	0.03931	1.465	0.124	1.464	0.0344	0.00009	0.121	0.135
2	0.06046	0.08005	1.186	0.247	1.183	0.0656	0.00005	0.240	0.251
3	0.1040	0.09459	1.198	0.300	1.196	0.0637	0.00005	0.297	0.244
4	0.1561	0.1492	1.057	0.394	1.052	0.0887	0.00003	0.387	0.333
5	0.1013	0.1940	0.858	0.547	0.846	0.1425	-	0.508	0.503
6	0.1432	0.2932	0.715	0.702	0.696	0.202	-	0.635	0.662
7	0.2140	0.4769	0.570	0.971	0.535	0.292	-	0.865	0.854

Co(II): logK₁ 1.15, logβ₂ 1.7, logβ₃ 1.4

1	0.0357	0.03692	1.592	0.321	1.591	0.02564	0.00012	0.319	0.305
2	0.0907	0.09623	1.306	0.517	1.302	0.0499	0.00006	0.512	0.522
3	0.03465	0.09662	1.147	0.732	1.140	0.0725	0.00004	0.698	0.681
4	0.2480	0.4008	0.876	1.079	0.845	0.1430	-	1.039	1.027
5	0.1387	0.3505	0.758	1.268	0.729	0.1868	-	1.180	1.174
6	0.2480	0.6498	0.579	1.559	0.522	0.3008	-	1.406	1.436

Ni(II): logK₁ 1.78, logβ₂ 3.0, logβ₃ 3.3, logβ₄ 3.0, logβ₅ (2.7)

1	0.04132	0.01724	2.252	0.283	2.252	0.00560	0.00053	0.283	0.292
2	0.04416	0.03727	1.903	0.569	1.902	0.01252	0.00024	0.568	0.563
3	0.09794	0.09677	1.697	0.784	1.692	0.0203	0.00015	0.782	0.776
4	0.04336	0.09548	1.370	1.220	1.363	0.0434	0.00007	1.204	1.209
5	0.1492	0.3312	1.069	1.647	1.038	0.0915	0.00004	1.606	1.635
6	0.1519	0.3867	0.961	1.826	0.925	0.1189	0.00003	1.763	1.776
7	0.1824	0.4714	0.914	1.916	0.868	0.1355	-	1.840	1.848
8	0.2387	1.0068	0.494	2.875	0.393	0.405	-	2.522	2.450
9	0.2565	1.290	0.356	3.310	0.226	0.595	-	2.710	2.683
10	0.2550	1.481	0.273	3.717	0.122	0.755	-	2.846	2.823

Zn(II): logK₁ 0.98, logβ₂ 1.45, logβ₃ 1.6, logβ₄ 1.4

1	0.03985	0.01806	1.866	0.117	1.867	0.01360	0.00022	0.117	0.124
2	0.02851	0.03659	1.538	0.270	1.537	0.0291	0.00010	0.266	0.249
3	0.1016	0.09606	1.291	0.442	1.288	0.0515	0.00006	0.439	0.416
4	0.02850	0.09676	1.101	0.616	1.094	0.0805	0.00004	0.572	0.596
5	0.09946	0.1946	0.971	0.882	0.957	0.1104	0.00003	0.847	0.770
6	0.1500	0.3479	0.768	1.182	0.740	0.182	-	1.106	1.100
7	0.2013	0.5835	0.589	1.619	0.538	0.290	-	1.458	1.476
8	0.1300	0.6303	0.439	2.050	0.3835	0.4135	-	1.669	1.797
9	0.2473	0.9775	0.381	2.271	0.290	0.513	-	1.879	1.998
10	0.1312	0.8604	0.327	2.962	0.248	0.565	-	2.251	2.086

Cd(II): logK₁ 1.30, logβ₂ 2.14, logβ₃ 2.5, logβ₄ 2.3

1	0.0402	0.01702	2.008	0.187	2.009	0.00980	0.00031	0.187	0.183
2	0.03965	0.03665	1.656	0.371	1.655	0.02212	0.0014	0.370	0.386
3	0.1006	0.09550	1.448	0.594	1.444	0.0360	0.00008	0.591	0.582
4	0.03976	0.09589	1.211	0.867	1.204	0.0625	0.00005	0.842	0.887
5	0.1004	0.1943	1.081	1.110	1.066	0.0860	0.00004	1.079	1.102
6	0.1790	0.3452	0.981	1.345	0.951	0.1120	0.00003	1.302	1.299
7	0.2776	0.6021	0.858	1.670	0.802	0.1578	-	1.600	1.567
8	0.1599	0.4849	0.749	1.918	0.703	0.1981	-	1.793	1.750
9	0.2785	0.7783	0.692	2.065	0.615	0.2426	-	1.923	1.913
10	0.2228	0.6945	0.657	2.128	0.589	0.2577	-	1.960	1.961

centration is given as the added molar concentration corrected for eventual excess of acid in the metal(II) stock solutions, and for non-equivalence of acid or base in the pyridinium nitrate stock solution. The hydrogen ion concentration is in most cases very small compared with the concentration of free pyridine, but is corrected for by means of $pK_{\text{pyH}^+} = 5.21$.⁴ For comparison, the 5th column of Table 1 gives the values for the ligand number \bar{n}' as calculated without correction for salt effects, as most authors do, by inserting a_{py}' for [py] in (4).

The cumulative stability constants stated in Table 1 are computed using mass action expressions with concentrations inserted for the metal ions, but as discussed in the preceding papers^{4,5} with the value of a_{py}' for $C_{\text{M}} = 0$, inserted instead of [py]. For comparison the last column of Table 1 gives the values for the ligand number, \bar{n}_{calc} , as calculated from the estimated stability constants for the values of $a_{\text{py}}' = [\text{py}]10^{0.082[\text{py}]}$ in question.

The agreement between the two sets of ligand numbers is on the whole satisfactory. This is also seen from Fig. 1 in which the formation curves are drawn through the calculated points. However, it must be considered that the

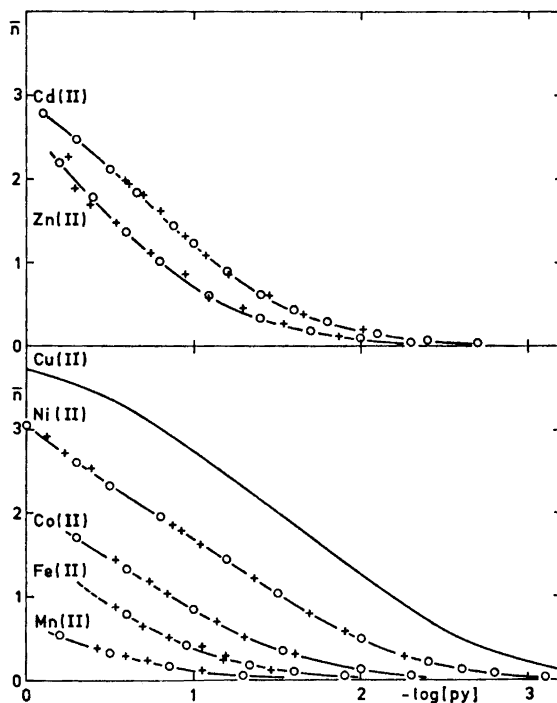


Fig. 1. Formation curves (\bar{n} vs. $-\log [\text{py}]$) for the metal(II) pyridine systems studied in 0.5 M pyHNO_3 at 25°C. The upper part of the figure is for zinc and cadmium, and the lower part is for divalent manganese iron, cobalt, and nickel. For comparison the curve for the copper(II) pyridine system⁴ is also given. +, experimental points; O, calculated points.

derived concentrations of free pyridine have a relatively high uncertainty. The uncertainty on \bar{n}_{exp} , and consequently also on the calculated constants, are therefore rather high. The $\log \beta_n$ constants for the higher complexes are for this reason only shown to one decimal place.

DISCUSSION

In Table 2 the logarithm of the consecutive constants, $\log K_n$, as calculated in this paper are compared with the previously published values^{1,2} as well as with newer data from the literature. The abbreviations used in the table are the same as in the Tables of Stability Constants.² It will be seen that the recalculated values in this paper (73 B) agree well with the earlier published values, but that more of the consecutive constants have been estimated in this paper. Comparison with the constants of other authors⁸⁻¹⁷ determined under similar conditions shows that $\log K_1$ and $\log K_2$ as a whole are in fair agreement if one does not include the much too high values found by Atkinson and Bau-

Table 2. Comparison of stepwise pyridine stability constants.

Ion	Method	Temp.	Medium	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	Ref.
In ²⁺	gl	25	0.5 pyHNO ₃	0.14					50 B ^{1,3}
	gl	25	0.5 pyHNO ₃	0.14	-0.5				73 B
	gl	25	1 NaClO ₄	1.86	1.6	0.9	0.6		63 A ⁶
Ce ²⁺	gl	25	0.5 pyHNO ₃	0.71					50 B ^{1,3}
	gl	25	0.5 pyHNO ₃	0.6	0.3				73 B
Co ²⁺	gl	25	0.5 pyHNO ₃	1.14	0.4				50 B ^{1,3}
	gl	25	0.5 pyHNO ₃	1.15	0.55	-0.3			73 B
	gl, dist	20	1 NH ₄ NO ₃	1.35	0.60	0.3	0.1		66 F ⁸
Ni ²⁺	gl	25	0.5 pyHNO ₃	1.78	1.05	0.3			50 B ^{1,3}
	gl	25	0.5 pyHNO ₃	1.83	1.2				59 A ¹⁰
	gl	25	0.5 pyHNO ₃	1.78	1.22	0.3	-0.3	(-0.3)	73 B
	gl	25	0.5 LiClO ₄	1.88	1.20				70 F ¹¹
	gl	25	0.6 KNO ₃	1.91	1.28	0.5			67 S ¹²
	gl	25	0.1 NaClO ₄	1.85					64 K ¹³
	gl, dist	20	1 NH ₄ NO ₃	1.98	1.04	0.4	0.0		66 F ⁸
n ²⁺	gl	25	1 NaClO ₄	2.13	1.66	1.1	0.6		63 A ⁶
	gl	25	0.5 pyHNO ₃	0.95	0.50				50 B ^{1,3}
	gl	25	0.5 pyHNO ₃	0.98	0.47	0.15	-0.2		73 B
	gl	25	0.5 LiClO ₄	0.99	0.28				70 F ¹¹
	gl	25	0.1 NaClO ₄	1.07					64 K ¹³
	Zn, Hg	30	0.1 NaClO ₄	1.10	0.61	0.2			66 D ¹⁴
d ²⁺	gl, dist	20	1 NH ₄ NO ₃	1.45	0.56	-0.2	0.3		67 F ⁸
	gl	25	1 NaClO ₄	2.08	1.69	1.0	0.6		63 A ⁶
	gl	25	0.5 pyHNO ₃	1.27	0.80				50 B ^{1,3}
Cd, Hg	gl	25	0.5 pyHNO ₃	1.30	0.84	0.36	-0.2		73 B
	gl	25	0.5 pyHNO ₃	1.28	0.74				71 B ¹⁵
	Cd, Hg	25	0.1 KNO ₃	1.28	0.74				71 B ¹⁵
	pol	30	0.1 KNO ₃	1.36	0.50	0.04			65 S ¹⁶
	qh, Hg	30	1 NaClO ₄	1.26	0.69	0.34			61 D ¹⁷
	gl, dist	20	1 NH ₄ NO ₃	1.51	0.95				67 F ⁸
									$\log \beta_4 = 2.50$

man.⁶ In the present paper in case of Ni^{2+} as much as 5, and in case of Zn^{2+} and Cd^{2+} as much as 4 consecutive constants were found necessary in order to obtain the best possible agreement with the experimental data in the accessible concentration range. Further it should be observed that the consecutive constants decrease with the number of pyridine molecules taken up as would be expected for systems of this kind.

The formation curves in Fig. 1 show that the stability of the complexes follow the natural order,¹⁸ *i.e.* increasing stability for the series of 1st transition group metal ions from Mn^{2+} to Cu^{2+} , and thereafter decreasing from Cu^{2+} to Zn^{2+} . For many zinc systems it is characteristic that the consecutive constants follow closer after each other than in the corresponding cadmium systems. The somewhat higher steepness of the zinc formation curve shows directly that this is also the case in the pyridine system.

Pyridine adducts of the 1st transition group metals of the type $\text{MX}_2 \cdot 6\text{py}$ have usually the constitution $[\text{M py}_4 \text{X}_2]$ with only 4 pyridine molecules coordinated to the metal ions, and with the remaining 2 pyridine molecules bound in the lattice.¹⁹ That this is a result of the weak coordinating properties of pyridine, and is not a steric property, is illustrated by the existence of the compound $[\text{Fe py}_6][\text{Fe}_4(\text{CO})_{13}]$, the structure of which has recently been determined.²⁰ Further evidence for the existence of octahedral hexapyridine complexes is given by Rosenthal and Drago,²¹ who in solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{py}$ in nitromethane have shown the existence of Ni py_6^{2+} . Herlocker and Rosenthal²² have also postulated the existence of Co py_6^{2+} , when $\text{Co}(\text{BF}_4)_2 \cdot 6\text{py}$ is dissolved in pyridine.

It is the opinion of the present author that the metal ions from Mn^{2+} to Ni^{2+} all tend to approach the formation of octahedral hexapyridine complexes. The zinc and cadmium ions similarly must be assumed to approach tetrahedrally built tetrapyridine complexes.

In conclusion it may be said that when the complex formation cannot be completed in aqueous solution, it is because of the relatively weak coordinating properties of pyridine combined with the fact that the decrease in dielectric constant with increasing pyridine concentration ($\epsilon = 12.3$ in pure pyridine) strongly favours the tendency to inner sphere complex formation with the anions present.

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