

Protonation of 1,2-Diamino-2-methyl-propane and Its Tendency to Form Copper Complexes in Aqueous Solution

REINO NÄSÄNEN and MARJATTA KOSKINEN

Department of Chemistry, University of Helsinki, Helsinki, Finland

The work on the acid dissociation of the protonated diamines and their copper complexes has been continued. The values $10^{-9.85}$ and $10^{-9.82}$ were obtained for the thermodynamic acid dissociation constants of diprotonated 1,2-diamino-2-methylpropane, denoted H_2L^{2+} , at 25°C. The electrolyte effect was studied with sodium perchlorate. The stability constants of CuL^{2+} and CuL_2^{2+} in sodium perchlorate solutions were determined. The values $10^{10.40}$ and $10^{9.07}$ were derived for the stepwise constants at zero ionic strength and 25°C. The results are discussed in relation to the respective properties of ethylenediamine and 1,2-diaminopropane.

This extension of earlier work¹ on the protonation and metal complex formation of some C-substituted ethylenediamines was undertaken in order to find out the effect of methyl groups in the series ethylenediamine, 1,2-diaminopropane and 1,2-diamino-2-methyl-propane.

The experimental methods¹ have been described earlier. The chemicals used were of the highest commercially available grades. The 1,2-diamino-2-methyl-propane, a product of Aldrich Chemical Co., was converted to its dihydrochloride which was recrystallized from methanol; m.p. 301–303°C.²

The acid dissociation constants defined by

$$K_1 = [H][HL]/[H_2L] \text{ and } K_2 = [H][L]/[HL] \quad (1)$$

where L denotes 1,2-diamino-2-methyl-propane were determined potentiometrically by the method described previously.¹ The results are collected in Table 1 and typical titration data are given in Table 2. The total concentration of $H_2L(ClO_4)_2$ is denoted by c and the total concentration of sodium hydroxide by c_B .

The variation of the first acid dissociation constant with ionic strength can be expressed by the equation

$$pK_1 = pK_1^0 + \frac{1.018\sqrt{I}}{1 + \alpha\sqrt{I}} + BI \quad (2)$$

Table 1. First and second acid dissociation constants of protonated 1,2-diamino-2-methylpropane at 25°C. Ionic strength adjusted with sodium perchlorate.

\sqrt{I}	pK_1	I	pK_2
0.154	6.374	0.018	9.83
0.187	6.402	0.025	9.83
0.213	6.427	0.031	9.83
0.724	6.862	0.518	9.98
0.731	6.705	0.525	9.97
0.739	6.703	0.531	9.97
1.012	6.862	1.018	10.12
1.017	6.852	1.025	10.10
1.023	6.851	1.031	10.10
1.423	7.076	2.018	10.32
1.427	7.079	2.025	10.31
1.430	7.070	2.031	10.32

Table 2. Evaluation of the acid dissociation constants of protonated 1,2-diamino-2-methylpropane from potentiometric titration data at 25°C. $I = 0.54$.

c_B/c	pK_1	c_B/c	pK_2
0.2	6.700	1.2	9.971
0.3	6.700	1.3	9.969
0.4	6.708	1.4	9.966
0.5	6.704	1.5	9.967
0.6	6.700	1.6	9.969
0.7	6.706	1.7	9.968
0.8	6.709	1.8	9.967
0.9	6.698		

Table 3. Parameters pK_1^0 , a and B of eqn. (2) and pK_2^0 , A , B , and C of eqn. (3) for ethylenediamine, 1,2-diaminopropane and 1,2-diamino-2-methylpropane.

	pK_1^0	a	B	pK_2^0	A	B	C
Ethylenediamine	6.837	1.381	0.209	9.933	0.308	—	—
1,2-Diaminopropane	6.607	1.420	0.180	9.817	0.410	-0.1218	0.0186
1,2-Diamino-2-methylpropane	6.246	1.383	0.169	9.820	0.297	0.0287	-0.046

and that of the second dissociation constant by the equation

$$pK_2 = pK_2^0 + AI + BI^{1.5} + CI^2 \quad (3)$$

The values of the parameters in eqns. (2) and (3) were calculated by the method of least squares from the data of Table 1. In the case of (3), pK_2^0 was first computed from data at $I < 1.0$ assuming $B = C = 0$. Thereafter the values of the parameters A , B , and C were calculated from all the data. The values of the para-

Table 4. Evaluation of the equilibrium constants K_I and K_{II} of copper 1,2-diamino-2-methyl-propane complexes at 25°C. $I = 0.559$.

c_B/c_M	pK_I	c_B/c_M	pK_{II}
0.2	6.040	1.2	7.268
0.4	6.041	1.4	7.259
0.6	6.041	1.6	7.271
0.8	6.026	1.8	7.273
1.0	6.023	2.0	7.274
1.2	6.029	2.2	7.268
1.4	6.038	2.4	7.268
1.6	6.022	2.6	7.270
1.8	6.031		

Table 5. Evaluation of the thermodynamic stepwise constants k_1^0 and k_2^0 of copper complexes of 1,2-diamino-2-methyl-propane at 25°C.

I	pK_I	pK_1	pK_2	$\log k_1$	I	pK_{II}	pK_1	pK_2	$\log k_2$
0.035	5.845	6.404	9.830	10.389	0.031	7.156	6.396	9.829	9.069
0.069	5.858	6.454	9.841	10.437	0.059	7.159	6.441	9.838	9.120
0.105	5.865	6.492	9.852	10.479	0.081	7.175	6.468	9.845	9.138
0.570	6.035	6.718	9.986	10.669	0.557	7.277	6.714	9.996	9.433
1.069	6.104	6.860	10.117	10.873	1.057	7.351	6.857	10.114	9.620
2.071	6.294	7.086	10.324	11.116	2.056	7.472	7.083	10.321	9.932

meters are given in Table 3 with the respective values for ethylenediamine and 1,2-diaminopropane.

Substitution of methyl groups on the carbon atoms of ethylenediamine is seen to decrease the base strength of the amine. The value of pK_1^0 for 1,2-diaminopropane is 0.23 log unit, and that for 1,2-diamino-2-methylpropane 0.59 log unit smaller than the value for ethylenediamine. The value of pK_2^0 decreases less, 0.12 log unit, in the case of both 1,2-diaminopropane and 1,2-diamino-2-methyl-propane. The electrolyte effect decreases in the same sequence, $pK_1 - pK_1^0$ being 0.90, 0.84 and 0.82, respectively, and $pK_2 - pK_2^0$ 0.62, 0.55 and 0.49, respectively at ionic strength 2.

Copper complex formation by 1,2-diamino-2-methyl-propane can be explained by the formation of CuL^{2+} and CuL_2^{2+} . The formation of $CuOHL^+$, $Cu_2(OH)_2L_2^{2+}$ and $Cu(OH)_2L$ cannot be studied in this case because of precipitation and does not obviously interfere in the determination of the stability constants. For the determination of the stepwise constants

$$k_1 = [ML]/[M][L] \text{ and } k_2 = [ML_2]/[ML][L] \quad (4)$$

several measurements were performed on solutions of varying concentration and ionic strength. Illustrative data from one titration are given in Table 4 together with respective values of the constants

$$K_I = [CuL][H]^2/[Cu][H_2L] \text{ and } K_{II} = [CuL_2][H]^2/[CuL][H_2L] \quad (5)$$

Table 6. Parameters of equation (7) for the stepwise stability constants of ethylenediamine, 1,2-diaminopropane, and 1,2-diamino-2-methyl-propane complexes of copper at 25°C.

	$\log k_1^0$	A	B	C	$\log k_2^0$	A	B	C
Ethylenediamine	10.48	0.646	-0.254	0.052	9.07	0.626	0.122	-0.202
1,2-Diaminopropane	10.56	0.890	-0.520	0.130	9.08	1.220	-0.720	0.150
1,2-Diamino-2-methyl-propane	10.40	0.404	0.234	-0.190	9.07	1.261	-1.050	0.324

The stepwise constants were calculated from

$$k_1 = K_I/K_1K_2 \quad \text{and} \quad k_2 = K_{II}/K_1K_2 \quad (6)$$

The evaluated stability constants are given in Table 5. They can be represented by the equation

$$\log k = \log k^0 + AI + BI^{1.5} + CI^2 \quad (7)$$

Values of the parameters of eqn. (7) calculated in the same way as those of eqn. (3) are given in Table 6 together with the respective values of ethylenediamine and 1,2-diaminopropane.

Substitution of methyl groups on the carbon atoms of ethylene-diamine is seen to affect the stability constants only slightly, $\log k_1^0$ being 0.08 log unit greater for 1,2-diaminopropane and 0.08 log unit smaller for 1,2-diamino-2-methyl-propane than for ethylenediamine. The values of k_2^0 are practically equal for all three compounds. The electrolyte effect is greatest for 1,2-diaminopropane. In the case of k_1^0 it increases in the order 1,2-diamino-2-methyl-propane, ethylenediamine, 1,2-diaminopropane $\log k_1 - \log k_1^0$ being 0.71, 0.78 and 0.83, respectively, at ionic strength 2. In the case of k_2^0 the sequence is: ethylenediamine, 1,2-diamino-2-methyl-propane, 1,2-diaminopropane, $\log k_2 - \log k_2^0$ being 0.79, 0.85, and 1.00, respectively, at ionic strength 2.

The ionisation of 1,2-diamino-2-methyl-propane and its copper complexes have been studied before.³ However, the measurements refer to a different ionic environment (0.5 M $\text{KNO}_3 + 0.05 \text{ M Ba}(\text{NO}_3)_2$) and comparison is useless.

REFERENCES

1. Näsänen, R. *Suomen Kemistilehti* **B 34** (1961) 4; Näsänen R. and Meriläinen, P. *Ibid.* **B 34** (1961) 47; **B 36** (1963) 97; Näsänen, R., Meriläinen, P. and Koskinen, M. *Ibid.* **B 35** (1962) 59; **B 36** (1963) 9; Näsänen, R., Meriläinen, P. and Lukkari, S. *Ibid.* **B 36** (1963) 135; **B 37** (1964) 1.
2. Cf. Stark, E. and Schwaneberg, H. *Ber.* **66** (1933) 1333.
3. Basolo, F., Murmann, R. K. and Chen, Y. T. *J. Am. Chem. Soc.* **75** (1953) 1478; **76** (1954) 956.

Received May 6, 1964.