

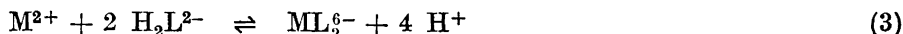
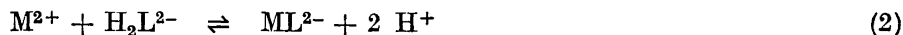
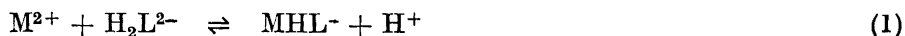
Studies on Some Metal Complexes of Catechol-3,5-disulphonic Acid

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The investigation of the complex formation of catechol-3,5-disulphonic acid with divalent metals has been continued. The data obtained by the pH method on the lead complexes can be explained satisfactorily by postulating the formation of the complexes PbHL^- and PbL_2^{2-} where L is the ligand. The formation of PbL_3^{6-} could not be established by the method used. The respective equilibrium constants were calculated. The formation of copper complexes was reinvestigated. In addition to the complexes CuL^{2-} and CuL_2^{6-} previously studied by the present author, the complex CuHL^- is obviously also formed at low ionic strengths, but in 1 M sodium perchlorate solution no such ion could be detected. The respective equilibrium constants have been calculated. The complexes formed between catecholdisulphonic acid and six divalent metals hitherto studied by the present author are discussed.

The complex formation of catechol-3,5-disulphonic acid with divalent metals is generally considered to involve the reactions ^{1,5}:



The role of the first reaction has been found to be relatively slight in all cases studied hitherto. In 1 M sodium perchlorate solution the measurements relating to the copper complexes did not even show any formation of the complex MHL^- , as will be described below. The third equilibrium is important only in the cases of zinc and copper.

Reactions (1) and (2) overlap when $c_B < 2c_M$ and the equilibrium constants defined by

$$K_H = [\text{MHL}^-] / [\text{ML}^{2-}] [\text{H}^+] \quad (4)$$

and

$$K_I = [\text{ML}^{2-}] [\text{H}^+]^2 / [\text{M}^{2+}] [\text{H}_2\text{L}^{2-}] \quad (5)$$

can be calculated from the equation

$$1/K_I = (1 + K_H [\text{H}^+]) (c_M - c') / c' + K_{II} (2c_M - c') x^2 / c', \quad (6)$$

where c_M is the total metal concentration, $c' = c - [\text{H}_2\text{L}^{2-}] (1 + K_s / [\text{H}^+])$ and $x = [\text{H}_2\text{L}^{2-}] / [\text{H}^+]^2$. The concentration of H_2L^{2-} is obtained from

$$[\text{H}_2\text{L}^{2-}] = (2c - c_B - [\text{H}^+] - [\text{MHL}^-]) / (2 + K_s / [\text{H}^+]) \quad (7)$$

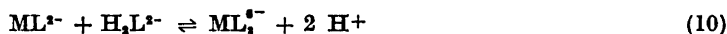
and

$$[\text{MHL}^-] = c' [\text{H}^+] K_H / (1 + K_H [\text{H}^+] + 2 K_{II} x), \quad (8)$$

where c and c_B are the total concentrations of $\text{Na}_2\text{H}_2\text{L}$ and sodium hydroxide, respectively. The constant K_s is defined by

$$K_s = [\text{H}^+] [\text{HL}^{2-}] / [\text{H}_2\text{L}^{2-}] \quad (9)$$

The second term of eqn (6) is negligible when the ionic strength is low and $c_B < 2c_M$, but in 1 M NaClO_4 it must be taken into account since the equilibrium constant K_{II} of the reaction



increases very greatly with ionic strength. The details of the calculation of the constants K_I and K_H have been described previously¹.

The constant K_{II}

defined by

$$K_{II} = [\text{ML}_2^{4-}] [\text{H}^+]^2 / [\text{ML}^{2-}] [\text{H}_2\text{L}^{2-}] \quad (11)$$

can also be calculated by means of eqn (6), which in this case is best used in the form

$$K_{II} = \frac{(1 + K_H [\text{H}^+]) (c' - c_M)}{x (2c_M - c')} + \frac{c'}{K_I x^2 (2c_M - c')} \quad (12)$$

The calculation of K_{II} is, of course, possible only when $2c_M < c_B < 4c_M$ and $c_M \leq 2c$. The second term of eqn (12) is negligible at low ionic strengths, but must be taken into account in 1 M NaClO_4 . The term $K_H [\text{H}^+]$ has been found to be negligible in the calculation of K_{II} .

EXPERIMENTAL

Beckman glass electrodes, types 4990-83 and E-2 were used. As reference electrode a calomel electrode was employed. When no neutral salt had been added to the solution studied, the electrode vessel and bridge were filled with a saturated solution of potassium chloride. When the solution to be measured was 1 M in sodium perchlorate, the electrode vessel and bridge were filled with a 1 M NaCl solution. In the former case a 0.05 M solution of potassium hydrogen phthalate, $\text{pH} = 4.01$, and in the latter case an acetate buffer

Table 1. Determination of hydrogen ion concentration of the acetate buffer at 25°C.

Solutions of hydrochloric acid, 1 M in NaClO ₄		Acetate buffer, 0.005 M in acetic acid, 0.005 M in sodium acetate, 1 M in NaClO ₄	
—log [H ⁺]	E mV	E mV	—log [H ⁺]
2.71	203.5	90.3	4.62
2.54	214.2	90.3	4.63
2.42	221.2	90.3	4.63
2.32	227.0	90.3	4.63

1 M in NaClO₄, served as standard buffer solutions. The acetate buffer was 0.005 M in acetic acid and in sodium acetate. Its hydrogen ion concentration was determined by means of a series of hydrochloric acid solutions, 1 M in NaClO₄, to be 10^{-4.63}. The acid dissociation constant of acetic acid should thus be 10^{-4.63} in 1 M NaClO₄. The results are given in Table 1. For this constant Ellilä² has obtained the value 10^{-4.61}. When a saturated calomel electrode was used, the pH values were converted to —log [H⁺] values by using the apparent p*f*_{H+} values³.

The chemicals used were of analytical grade. In potentiometric measurements a Radiometer PHM 3 m potentiometer_A was used.

RESULTS AND DISCUSSION

The values obtained for the constants *K*_H and *K*_I in the cases of copper and lead without addition of a neutral salt are given in Table 2. The data previously obtained for cadmium, cobalt, nickel and zinc complexes have been included. The respective values at zero ionic strength are given in Table 3.

Table 2. Equilibrium constants relating to the complex formation by some metals with catecholdisulphonic acid at 25°C. Complexes MHL⁻ and ML²⁻.

c:cm	√ <i>I</i>	log <i>K</i> _H											
		Cd	Co	p <i>K</i> _I Ni	Zn	Pb	Cu	Cd	Co	Ni	Zn	Pb	Cu
1:1	0.088	11.16	10.65	10.21	9.75	6.72	5.85	6.88	—	—	5.8b	—	3.54
2:1	0.108	11.19	10.70	10.25	9.80	6.74	5.87	6.84	—	—	5.82	—	3.48
3.33:1	0.129	11.19	10.72	—	9.84	6.72	5.88	6.78	—	—	5.74	—	3.40
6.67:1	0.170	11.24	10.75	10.29	9.84	—	—	6.74	—	—	5.68	—	—
mean value	(0.124)	11.20	10.71	10.25	9.81	6.72	5.87	6.81	6.48	6.00	5.79	4.46	3.47

Table 3. Equilibrium constants relating to the complex formation by some metals with catecholdisulphonic acid at 25°C and at zero ionic strength.

	p <i>K</i> _I ^o	log <i>K</i> _H ^o	log <i>K</i> _M ^o	log β ₁ ^o
Cd	11.09	7.01	4.23	10.29
Co	10.60	6.68	4.39	10.78
Ni	10.14	6.20	4.37	11.24
Zn	9.70	5.99	4.58	11.68
Pb	6.61	4.66	6.36	14.77
Cu	5.76	3.67	6.22	15.62

In extrapolating, the equation

$$pK_I = pK_I^{\circ} + \frac{1.018 \sqrt{I}}{1 + 2.0 \sqrt{I}} \quad (12)$$

obtained earlier for the respective copper complex was used¹. The constant K_H was correspondingly extrapolated to zero ionic strength by means of the equation

$$\log K_H = \log K_H^{\circ} - \frac{2.04 \sqrt{I}}{1 + 2 \sqrt{I}} \quad (13)$$

Table 3 also contains the values of the stability constant

$$\beta_1^{\circ} = (ML^{2-})/(M^{2+}) (L^{4-}) \quad (14)$$

as calculated from

$$\beta_1^{\circ} = K_I^{\circ}/K_3^{\circ} K_4^{\circ} \quad (15)$$

For the acid dissociation constants K_3° and K_4° the values $10^{-8.31}$ and $10^{-13.07}$ (25°C), taken from a previous paper by the present author⁴, were used. Further, the equilibrium constants of the reaction



defined by

$$K_M^{\circ} = (MHL^{-})/(M^{2+}) (HL^{3-}) \quad (17)$$

are given in Table 3. This constant can be calculated from the expression

$$K_M^{\circ} = K_H^{\circ} K_I^{\circ}/K_3^{\circ} \quad (18)$$

Recently the values of β_1 , K_M , K_3 and K_4 in 0.1 M KCl determined for some metals by Schwarzenbach and Willi have been published⁵. Since the value of K_4 determined by the present author differs considerably from that given by these authors, the comparison of the K_I and K_H values seemed to be more suitable than of the β_1 and K_M values. Therefore the values of K_I and K_H

Table 4. The constants K_3 , K_4 , K_H and K_I in 0.1 M KCl.

	pK_3	pK_4	Cd	Co	Ni	pK_I	Zn	Pb	Cu
Schwarzenbach and Willi ⁵ (20°C)	7.66	12.6	—	10.77	10.30	9.85	—	—	5.73
Present author (25°C)	7.64	12.2	11.29	10.80	10.34	9.90	6.81	—	5.96
						$\log K_H$			
Schwarzenbach and Willi (20°C)			Cd	Co	Ni	Zn	Pb		Cu
Present author (25°C)			6.61	6.28	5.80	5.59	4.26	—	3.27

Table 5. Determination of the constant K_{II} for the complex CuL_2^{6-} at 25°C.

\sqrt{I}	$c \times 10^3$	$c_B \times 10^3$	$c_M \times 10^3$	$[H^+] \times 10^7$	$K_{II} \times 10^{11}$
0.137	4.219	2.954	1.266	4.20	0.82
0.142	4.211	3.158	1.263	3.22	0.85
0.148	4.202	3.361	1.261	2.61	0.90
0.153	4.193	3.564	1.258	2.15	0.91
0.159	4.184	3.766	1.255	1.79	0.90
0.163	4.175	3.967	1.253	1.513	0.89
0.168	4.167	4.167	1.250	1.265	0.85
0.173	4.158	4.366	1.247	1.062	0.83
				mean value	0.87

were calculated from the data of Schwarzenbach and Willi. The respective values of K_I and K_H at ionic strength 0.1 were calculated from the data of the present author by means of eqns (12) and (13). These results are given in Table 4. The pK_I values of the Co, Ni and Zn complexes are seen to agree so well that the small differences, 0.03, 0.04 and 0.05, might be attributed mainly to a temperature effect. In the case of copper, however, a greater difference exists. The $\log K_H$ values differ more; 0.09, 0.16 and 0.10 in the cases of Co, Ni and Zn, respectively. Here again, some of the difference may be due to the different temperatures used, but on the other hand the accuracy that can be achieved is not very high, as already mentioned above. The agreement is thus very good if one leaves out of account the constant K_4 and the constants for the copper complexes.

From the data of the second buffer range at which $2c_M < c_B < 4c_M$ the values of the constant K_{II} can be evaluated. As mentioned above, only in the case of zinc and copper¹ could a distinct formation of ML_2^{2-} be observed. The stability of CuL_2^{6-} has been reinvestigated. In Table 5 a titration is shown. The quantity K_{II} is seen to remain nearly constant, although the increase in the concentration of the CuL_2^{6-} ion during the titration causes a considerable change in ionic strength as defined by $I = \frac{1}{2} \sum z_i^2 c_i$. An equal change in ionic strength produced by addition of neutral salt has a considerable effect on the quantity K_{II} ¹. A similar state of affairs has previously been shown

Table 6. Determination of the constant K_I for the complex CuL^{2-} at 25°C and in 1 M $NaClO_4$.

$c \times 10^3$	$c_B \times 10^3$	$c_M \times 10^3$	$[H^+] \times 10^5$	$K_I \times 10^6$
4.329	0.433	1.299	12.02	0.95
4.320	0.648	1.296	9.90	0.98
4.310	0.862	1.293	8.51	1.07
4.301	1.075	1.290	7.08	1.03
4.292	1.288	1.288	6.03	1.05
4.283	1.499	1.285	5.13	1.05
4.274	1.709	1.282	4.27	1.01
4.264	1.919	1.279	3.55	1.00
4.256	2.128	1.277	2.95	0.99

Table 7. Determination of the constant K_I for the complex CuL_2^{2-} using different metal- $\text{Na}_2\text{H}_2\text{L}$ ratios at 25°C and in 1 M NaClO_4 .

$c:c_M$	pK_I
1:1	5.98
2:1	5.99
3.33:1	6.00
6.67:1	6.00

to prevail in the cases of the zinc¹ and aluminium⁶ complexes. Regarding the effect of added electrolytes, the sum of the concentrations of the positive ions, i.e. the quantity $\frac{1}{2}\sum z_i c_i$, seems to be the decisive factor and not $\frac{1}{2}\sum z_i^2 c_i$.

It is, of course, possible that in a medium containing sodium ions species such as $\text{Na}_\nu\text{ML}_2^{(6-\nu)-}$ are formed. If so, the quantity $[\text{ML}_2^{6-}]$ should in reality be a sum $\sum \text{Na}_\nu\text{ML}_2^{(6-\nu)-}$ and the quantity K_{II} a function of the sodium ion concentration of the form

$$K_{II} = K_{II}^{(0)} + K_{II}^{(1)}[\text{Na}^+] + K_{II}^{(2)}[\text{Na}^+]^2 + \dots \quad (19)$$

Since the quantity $K_{II}^{(\nu)}$ defined by

$$K_{II}^{(\nu)} = \frac{[\text{Na}_\nu\text{ML}_2^{(6-\nu)-}][\text{H}^+]^2}{[\text{ML}_2^{6-}][\text{H}_2\text{L}^{2-}][\text{Na}^+]^\nu} \quad (20)$$

is also obviously a function of ionic strength, the exact treatment of this contingency is not feasible. The experimental data seem to indicate, however, that at low ionic concentration the species ML_2^{6-} is the predominant one but that at a high concentration of sodium ions the species $\text{Na}_\nu\text{ML}_2^{(6-\nu)-}$ might also be formed.

Since the complex formation under investigation, especially the formation of ML_2^{6-} , is so highly dependent on the ionic medium it seemed advisable to investigate this system in a medium containing some neutral salt. Hitherto, only copper complexes have been investigated in this way. In Table 6 a titra-

Table 8. Determination of the constant K_{II} for the complex CuL_2^{6-} in 1 M NaClO_4 and at 25°C.

$c \times 10^3$	$c_B \times 10^3$	$c_M \times 10^3$	$[\text{H}^+] \times 10^5$	$K_{II} \times 10^8$
4.219	2.954	1.266	1.290	1.73
4.211	3.158	1.263	1.047	1.67
4.202	3.361	1.261	0.892	1.76
4.193	3.564	1.258	0.742	1.73
4.184	3.766	1.255	0.631	1.78
4.175	3.967	1.253	0.513	1.68
4.167	4.167	1.250	0.427	1.72
4.158	4.366	1.247	0.347	1.76
4.149	4.564	1.245	0.263	1.76

Table 9. Determination of the constant K_{II} for the complex CuL_2^{6-} using different metal- Na_2H_2L ratios in 1 M $NaClO_4$ and at 25°C.

c:cm	pK_{II}
2:1	7.82
3.33:1	7.76
6.67:1	7.78

tion for determination of the constant K_I for the copper complex in 1 M sodium perchlorate is given. In this case, the second term in eqn. (6) must also be considered, as already mentioned above. On the other hand, the formation of the complex $CuHL^-$ is so slight that it cannot be demonstrated. This is readily understandable in view of the fact that the equilibrium constant K_{II} decreases with increasing ionic strength and that the concentration of $CuHL^-$ is already small at low ionic strength. Titrations for the determination of K_I were carried out for four different Na_2H_2L -metal ratios. These results are given in Table 7 and it will be seen that the accuracy is even better than that reached in the measurements without addition of neutral salts. In Table 8 a titration for the determination of the constant K_{II} is given. The accuracy reached is seen to be very good in this case too. In eqn. (12) the second term must also be considered, because reactions (2) and (3) overlap somewhat. In Table 9 the results for K_{II} have been summarized.

For the constants K_I and K_{II} in the case of copper the present author obtained the values $pK_I = 6.08$ and $pK_{II} = 7.40$ in 1 M KCl. These values thus differ in an understandable way from the values $pK_I = 6.00$ and $pK_{II} = 7.79$ now obtained in 1 M $NaClO_4$.

The stability constants β_1 and β_2 for copper complexes are given in Table 10. The constant β_1 was calculated from eqn. (15) and the constant β_2 , defined by

$$\beta_2 = [CuL_2^{6-}]/[Cu^{2+}] [L^{4-}]^2, \quad (21)$$

from the expression

$$\beta_2 = K_I K_{II} / K_3^2 K_4^2 \quad (22)$$

The values of the acid dissociation constants K_3 and K_4 in 1 M $NaClO_4$ were determined in the same way as before, but the electrode system used was the same as in the study of complexes in 1 M $NaClO_4$. Somewhat unexpectedly, the values obtained for K_3 and K_4 in 1 M $NaClO_4$ are almost identical with those obtained for these constants in 1 M KCl.

Table 10. Stability constants of catechol-3,5-disulphonic acid chelates of copper in 1 M $NaClO_4$ and at 25°C.

$pK_3 = 7.19$;	$pK_I = 6.00$;	$\log \beta_1 = 12.79$
$pK_4 = 11.6$;	$pK_{II} = 7.79$;	$\log \beta_2 = 23.79$

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