

# Metal Complexes with Mixed Ligands. 26. Complex Formation between Cadmium(II) Imidazoles and Chloride Ions. A Potentiometric and Solubility Study in Mixed 3.0 M (Na)ClO<sub>4</sub>, Cl Media

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Stability constants of ternary Cd<sup>2+</sup>-complexes with the ligands imidazole (C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>,L) and chloride ions were studied at 25 °C. The measurements were performed as potentiometric titrations [glass and Cd(Hg) electrodes] in ionic media consisting of mixtures of 3.0 M (Na)ClO<sub>4</sub> and 3.0 M (Na)Cl. Besides pure binary species CdL<sub>n</sub><sup>2+</sup>, n=1, 2, 3, 4 and CdCl<sub>s</sub><sup>(2-s)+</sup>, s=1, 2, 3, data can be explained with the ternary complexes CdLCl<sup>+</sup>, CdLCl<sub>2</sub><sup>-</sup>, CdL<sub>2</sub>Cl<sup>+</sup>, CdL<sub>2</sub>Cl<sub>2</sub> and CdL<sub>3</sub>Cl<sup>+</sup> with formation constants log β<sub>111</sub>=4.33±0.01, log β<sub>113</sub>=5.11±0.06, log β<sub>121</sub>=6.26±0.03, log β<sub>122</sub>=6.57±0.06 and log β<sub>131</sub>=7.95±0.03. In addition, two stable solid phases were obtained, CdLCl<sub>2</sub>(s) with

$$\log \beta(\text{Cd}^{2+} + \text{L} + 2\text{Cl}^- \rightleftharpoons \text{CdLCl}_2(\text{s})) = 7.76 \pm 0.07$$

and CdL<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> with

$$\log \beta(\text{Cd}^{2+} + 6\text{L} + 2\text{ClO}_4^- \rightleftharpoons \text{CdL}_6(\text{ClO}_4)_2(\text{s})) = 13.8 \pm 0.2.$$

In the calculations the computer programs LETAGROPVRID and SOLGASWATER were employed.

Complexation in the Cd<sup>2+</sup>-imidazole (C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>,L)-OH<sup>-</sup> system was presented in a preceding publication.<sup>1</sup> By using glass and Cd(Hg) electrodes it was shown that besides pure binary species, CdL<sub>n</sub><sup>2+</sup> (n=1..4), a mixed hydroxo complex CdLOH<sup>+</sup> was formed. A comparison between acidities of the Cd<sup>2+</sup>- and

CdL<sup>2+</sup>-ions clearly showed CdL<sup>2+</sup> to be a stronger acid. This fact indicates that a coordinated imidazole ligand enhances the affinity for OH<sup>-</sup> in the complex. This behaviour has earlier been found in the corresponding Zn<sup>2+</sup> and Hg<sup>2+</sup> systems investigated by Forsling<sup>2</sup> and Sjöberg,<sup>3</sup> respectively. In these two systems the stability of several mixed Me<sup>2+</sup>-L-Cl<sup>-</sup> complexes was also evaluated.

It was also found, as in the case of ZnOH<sup>+</sup>, that ZnCl<sup>+</sup> is a stronger complexing agent to imidazole than the Zn<sup>2+</sup>-ion. In the mercury(II) system no pronounced enhancement for Cl<sup>-</sup> in the different Hg<sup>2+</sup>-L and Hg<sup>2+</sup>-L-Cl<sup>-</sup> complexes was found.

The aim of the present investigation was to determine compositions and stabilities of possible mixed chloro complexes in the Cd<sup>2+</sup>-L-Cl<sup>-</sup> system. Furthermore, the solubility products of crystalline precipitates, obtained during the experimental conditions, were determined.

By means of the results obtained, a comparison of stabilities of different binary and ternary complexes within the 2B group was performed.

## EXPERIMENTAL

*Chemicals and analysis.* All solutions used were prepared and analyzed as described earlier.<sup>1</sup> A protolytic impurity in 3 M NaClO<sub>4</sub> and 3 M NaCl solutions was determined amounting to 10<sup>-4</sup> M with an acidity constant of ~10<sup>-8</sup> M.

Corrections for this impurity have been made in the calculations described below.

**Method.** The titrations were performed as potentiometric titrations (glass and Cd(Hg) electrodes) at 25 °C. The titration procedures and the experimental details of the measurements are fully described in Ref. 1.

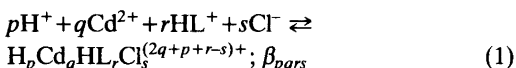
The equilibrium solutions were made to contain  $[\text{ClO}_4^-] + X = 3.0 \text{ M}$ , where X is the total concentration of chloride ions. The general compositions of solutions were: B M  $\text{Cd}^{2+}$ , C M  $\text{HL}^+$ , H M  $\text{H}^+$ , X M  $\text{Cl}^-$ ,  $(3.00 - X)$  M  $\text{ClO}_4^-$  and  $([\text{ClO}_4^-] + X - 2B - C - H)$  M  $\text{Na}^+$ . B, C and X are the total concentrations of cadmium(II), imidazole and chloride and H stands for the total concentration of protons calculated over the zero level  $\text{Cd}^{2+}$ ,  $\text{HL}^+$ ,  $\text{Cl}^-$  and  $\text{H}_2\text{O}$ . The free hydrogen ion concentration, h, and the free cadmium ion concentration, b, were measured with a glass electrode and a cadmium–amalgam electrode, respectively.

**Solid phases.** Most of the titrations were ended by the formation of crystalline precipitates. Three different phases were identified,  $\text{CdLCl}_2(\text{s})$ ,  $\text{CdL}_2\text{Cl}_2(\text{s})$  and  $\text{CdL}_6(\text{ClO}_4)_2(\text{s})$ , by using powder X-ray techniques.

The solid phase  $\text{CdL}_2\text{Cl}_2$  was transformed to  $\text{CdLCl}_2$  after a while. Due to this instability,  $\text{CdL}_2\text{Cl}_2$  was not further examined and no attempts were made to determine the solubility product for this phase.

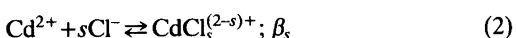
To determine the solubility products of  $\text{CdLCl}_2$  and  $\text{CdL}_6(\text{ClO}_4)_2$ , the solutions were equilibrated with these phases for several months, filtered and then analyzed with respect to H and the free concentrations of  $\text{Cd}^{2+}$  (b) and  $\text{Cl}^-$  (x). H in the solutions was determined by adding  $\text{H}^+$  from a burette and evaluated using a Gran<sup>4</sup> plot. b was determined by using a cadmium ion–selective electrode (Orion, model 94-48A) and x was measured by means of an Ag,AgCl electrode. In a few solutions x was too high to be accurately measured. Instead X was determined (precipitated as AgCl in acidified solutions) and x was calculated as described below.

**Speciation and equilibria.** We will assume the presence of four component equilibria of the general form



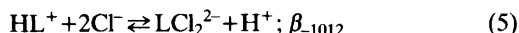
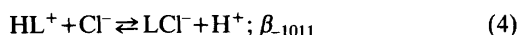
In addition to the four component equilibria we have:

(i) Complex formation between cadmium(II) and chloride



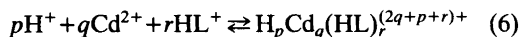
In 3.0 M (Na)ClO<sub>4</sub>,Cl medium the formation constants were determined to be  $\log \beta_1 = 1.55(1)$ ,  $\log \beta_2 = 2.19(2)$  and  $\log \beta_3 = 2.34(3)$ , in good agreement with those determined by Biedermann *et al.*<sup>5</sup> The equilibrium constant for the complex  $\text{CdCl}_4^{2-}$ ,  $\log \beta_4$ , turned out with great uncertainty. However, within the concentration range investigated the complex  $\text{CdCl}_4^{2-}$  could be neglected, and no further attempts to determine the value of the formation constant were made.

(ii) The imidazole equilibria, which within the concentration range  $0 \leq X \leq 3.0 \text{ M}$  with  $(\text{ClO}_4^- + X) = 3.0 \text{ M}$  are determined by Sjöberg,<sup>3</sup> and could be described as



with  $\log k_a = -7.913$ ,  $\log \beta_{-1011} = -8.641$  and  $\log \beta_{-1012} = -9.279$ .

(iii) The cadmium(II) imidazole equilibria<sup>1</sup>



with  $\log \beta_{-111} = -4.820$ ,  $\log \beta_{-212} = -10.327$ ,  $\log \beta_{-313} = -16.451$  and  $\log \beta_{-414} = -23.14$ .

In the present study the hydrolytic equilibria of the cadmium(II) ion as well as the formation of ternary cadmium(II)–OH<sup>-</sup>–imidazole complexes could be neglected provided  $C/B > 6$  or  $B \geq 0.010 \text{ M}$ . Equilibria (2)–(6) were assumed to be known in the calculations concerning the four component equilibria.

**Computer programs used.** The mathematical analysis of the experimental data were performed with the least-squares computer program LETAGROPVRID<sup>6</sup> (version ETITR<sup>7,8</sup>). As input to this program h, b, H, C and X or h, b, B, C and X were given. The error squares sums  $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$  and  $U = \sum (B_{\text{calc}} - B_{\text{exp}})^2$ , respectively, were minimized. The different standard deviations were defined and calculated according to Sillén.<sup>9,10</sup>

Calculations of the free concentrations of imidazole, [L], and chloride for obtaining the solubility products, were performed by using the computer program SOLGASWATER.<sup>11</sup> As input to this program b, H, X-data and formation constants  $\beta_{nqs}$  defined according to the equilibria



were given. [L] and x were then calculated using the expressions

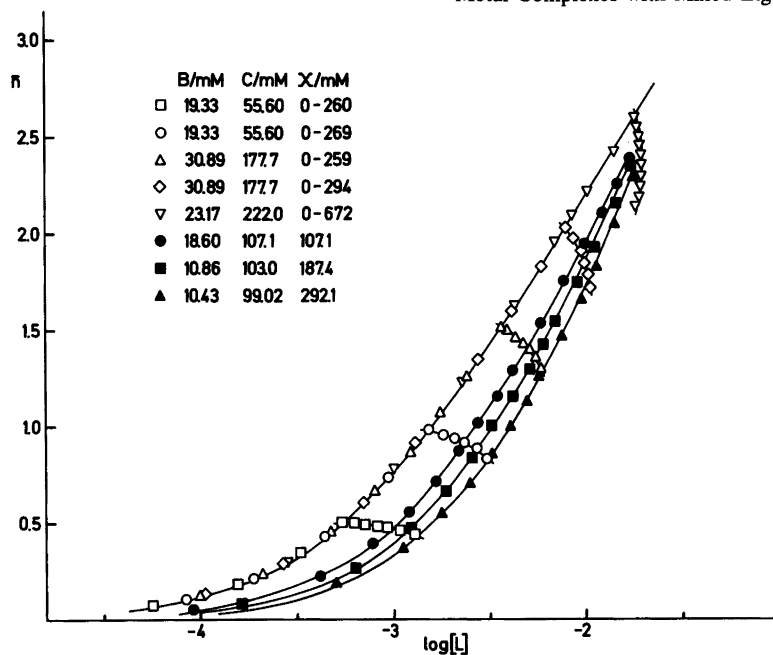


Fig. 1. Experimental data plotted as curves  $\bar{n}(\log [L])$ . Open symbols refer to titrations in 3.0 M (Na)ClO<sub>4</sub> and mixed media at defined  $\bar{n}$ -values. Filled symbols refer to titrations at constant Cl<sup>-</sup> concentrations. The full curves were calculated with  $\beta_n$  values given in the final model.

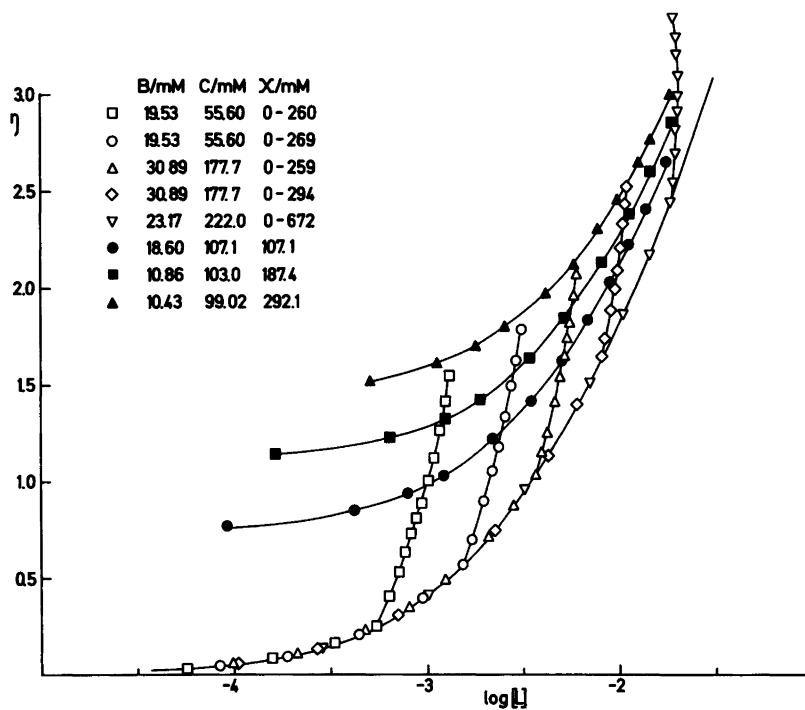
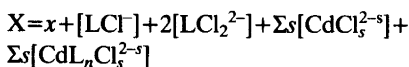
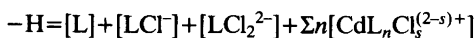


Fig. 2. Experimental data plotted as curves  $\eta(\log [L])$ .



The program SOLGASWATER was also used to calculate distribution diagrams and predominance area diagrams in order to visualize the amounts of the different species.

The mathematical analysis of powder X-ray data was performed using a least-squares program.<sup>12</sup> As input the cell parameters given in the structure determination of  $(CdLCl_2)_\infty$ <sup>13</sup> and  $(CdL_2Cl_2)_\infty$ <sup>14</sup> and those for  $CdL_6(ClO_4)_2$  were used. Clear evidence for the existence of these solid phases was given.

The computations were performed on a CD 6600 computer.

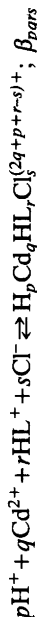
## DATA, CALCULATIONS AND RESULTS

Experimental data were collected by performing titrations with  $OH^-$  or  $H^+$  at constant  $Cl^-$  concentrations ( $X=0, 0.11, 0.15, 0.19, 0.22$  and  $0.3$  M) and at defined  $\bar{n}$  values ( $\bar{n}=0.25, 0.5, 0.75, 1, 1.2, 1.5, 1.7, 2, 2.3$  and  $2.6$ ) where solutions  $3.0$  M in  $(Na)ClO_4$  were titrated with solutions  $3.0$  M in  $(NaCl+NaClO_4)$ . The quotients  $C/B$  were kept constant and had the values  $3, 6$  and  $10$ . The concentration ranges investigated were  $4 < -\log h < 8, 0.01 \leq B \leq 0.03$  M,  $0.05 \leq C \leq 0.22$  M and  $0 < X \leq 0.6$  M, comprising 15 different titrations with 284 experimental points.

The analysis of data was started by making  $\bar{n}(\log [L])$  plots and  $\eta(\log [L])$  plots, by using  $E_H$  data and  $(E_B+E_H)$  data, respectively. These are shown in Figs. 1 and 2. Systematic deviations from the  $\bar{n}$  and  $\eta$  curves indicate formation of ternary mixed complexes of type  $Cd_qL_nCl_s^{(2q-s)+}$ .

The different LETAGROP calculations showed that the "best" explanation of the experimental data was obtained with the ternary complexes  $CdLCl^+$ ,  $CdLCl_3^-$ ,  $CdL_2Cl^+$ ,  $CdL_2Cl_2$  and  $CdL_3Cl^+$ . The complexes  $CdLCl_2$ ,  $CdLCl_4^{2-}$ ,  $CdL_2Cl_3^-$ ,  $CdL_3Cl_2$ ,  $CdL_4Cl^+$  and  $CdL_4Cl_2$  were also tested one at a time. Formation constants of these complexes came out with large standard deviations. The results of these calculations are summarized in Table 1. At higher  $Cl^-$  concentrations ( $2.25$  M) a titration was performed in order to find out whether there were any additional complexes formed at high  $Cl^-$  concentration. However, data could satisfactorily be explained

Table 1. Results of LETAGROP calculations concerning formation of ternary  $Cd^{2+}-L-Cl^-$  complexes. The formation constants are defined according to the equilibrium.



When no  $3\sigma(\log \beta_{pqrs})$  is given the formation constant has not been varied. R denotes a rejected complex ( $\beta_{pqrs} \leq 0$ ).

No. of titr/ No. of points	$CdLCl^+$ $\log(\beta_{-1111} \pm 3\sigma)$	$CdLCl_3^-$ $\log(\beta_{-1113} \pm 3\sigma)$	$CdL_2Cl^+$ $\log(\beta_{-2121} \pm 3\sigma)$	$CdL_2Cl_2$ $\log(\beta_{-2122} \pm 3\sigma)$	$CdL_3Cl^+$ $\log(\beta_{-3131} \pm 3\sigma)$	$CdL_nCl_s^{(2-s)+}$ $\log(\beta_{pqrs} \pm 3\sigma)$	$p, r, s$	$U^a$	$\sigma(y)$
15/284	-3.58(1)	-2.80(6)	-9.60(3)	-9.26(6)	-15.79(3)			2.93 <sup>c</sup>	0.10
	-3.60(2)	-2.84(5)	-9.50(5)	-9.29(5)	-15.82(9)			4.77 <sup>b</sup>	0.13
	-3.61(3)	-2.94(9)	-9.60	-9.29	-15.79			2.82	0.10
	-3.58(1)	-2.80(2)	-9.60	-9.29	-15.79	-3.77(14)	-1,1,2	2.93	0.10
	-3.58	-2.80	-9.60(2)	-9.28(10)	-15.79	R	-1,1,4	2.93	0.10
	-3.58	-2.80	-9.59(3)	-9.30(9)	-15.80(4)		-2,2,3	2.90	0.10
	-3.58	-2.80	-9.59(3)	-9.26(4)	-15.80(7)		-3,3,2	2.93	0.10
	-3.58	-2.80	-9.59(3)	-9.29(6)	-15.80(3)		-4,4,1	2.93	0.10
	-3.58	-2.80	-9.59(3)	-9.29(6)	-15.80(3)		-4,4,2	2.88	0.10

<sup>a</sup>  $Y=H_{CALC}-H_{EXP}$ . Calculations are based on  $E_H+E_B$  data with data set  $h, b, H, C, X$  used. <sup>b</sup>  $(Y)=B_{CALC}-B_{EXP}$ . Calculations are based on  $E_H+E_B$  data with data set  $h, b, B, C, X$  used. <sup>c</sup> Proposed constants. <sup>d</sup> Min and max values in  $\log \beta$ .

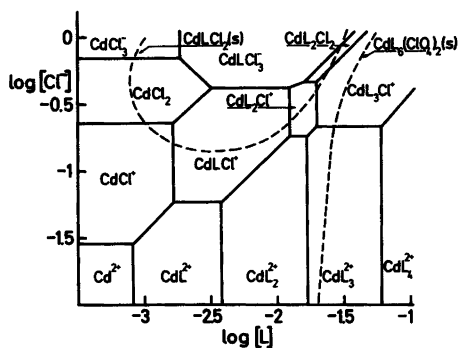


Fig. 3. Predominance area diagram for different cadmium(II) complexes and solid phases for  $B=0.01\text{ M}$ ,  $([\text{ClO}_4^-]+X)=3.0\text{ M}$ .  $\log [L] \geq -1.8$  and  $\log [\text{Cl}^-] \geq -0.4$  denote extrapolated ranges.

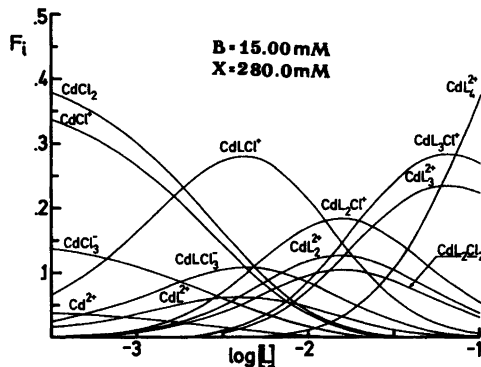
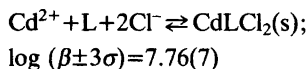


Fig. 4. Distribution diagram  $F_i(\log [L])_{B,X}$  for the different cadmium(II) complexes.

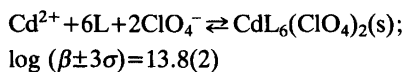
with the complex  $\text{CdLCl}_3^-$  besides the binary  $\text{CdCl}_s^{(2-s)+}$ ,  $s=1 \dots 4$ , complexes and no further measurements in this area up to  $3.0\text{ M Cl}^-$  were performed. (In this calculation  $\log \beta_4=2.2$  according to Biedermann<sup>5</sup> was used.)

In order to visualize the amounts of the different Cd(II) species in this system a distribution diagram as well as a predominance area diagram have been constructed (see Figs. 3 and 4).

For the solid phases  $\text{CdLCl}_2$  and  $\text{CdL}_6(\text{ClO}_4)_2$ , solutions were analyzed to determine their solubility products. The measurements include seven solutions for the phase  $\text{CdLCl}_2$  and three solutions for  $\text{CdL}_6(\text{ClO}_4)_2$ . The solubility products were defined according to the relation



and



As this determination is based on rather few data, the resulting standard deviations are quite large.

The extent to which the solid phases are formed is demonstrated in the predominance area diagram for  $B=0.01\text{ M}$  (Fig. 3).

### DISCUSSION

The present emf investigation has clearly shown the existence of ternary cadmium(II)-imidazole- $\text{Cl}^-$  complexes. Besides the series  $\text{CdL}_n\text{Cl}^+$ ,  $n=1, 2, 3$  the complexes  $\text{CdL}_2\text{Cl}_2$  and  $\text{CdLCl}_3^-$  were formed. These ternary complexes are all formed in significant amounts and do in fact predominate within specified ranges (*cf.* Fig. 3). The results can be interpreted as stepwise reactions in which  $\text{Cl}^-$  ions are successively coordinated to each of the  $\text{CdL}_n^{2+}$  species ( $n=0, 1, 2, 3$ ). Stepwise constants for the reactions

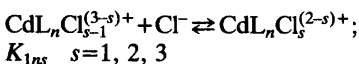


Table 2. Some stepwise reactions with constants calculated by means of formation constants given in this paper. The different reactions define the stepwise uptake of  $\text{Cl}^-$  and are to be read horizontally. ( $\text{CdL}^{2+} 1.24 \text{ CdLCl}^+$  stands for  $\text{CdL}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdLCl}^+$  with  $\log K=1.24$ .)

$\text{Cd}^{2+}$	1.55	$\text{CdCl}^+$	0.65	$\text{CdCl}_2$	0.15	$\text{CdCl}_3^-$
$\text{CdL}^{2+}$	1.24	$\text{CdLCl}^+$		0.78		$\text{CdLCl}_3^-$
$\text{CdL}_2^{2+}$	0.72	$\text{CdL}_2\text{Cl}^+$	0.35	$\text{CdL}_2\text{Cl}_2$		
$\text{CdL}_3^{2+}$	0.66	$\text{CdL}_3\text{Cl}^+$				

Table 3. Logarithms of the statistical stability constants of the complexes compared with the corresponding experimental stability constant.

Formula	Stat. value of $\log \beta_{ns}$	Exp. value of $\log \beta_{ns}$
CdLCl <sup>+</sup>	4.15	4.33
CdL <sub>2</sub> Cl <sup>+</sup>	6.12	6.24
CdL <sub>3</sub> Cl <sup>+</sup>	7.53	7.94
CdL <sub>2</sub> Cl <sub>2</sub>	6.13	6.57
CdLCl <sub>3</sub> <sup>-</sup>	4.38	5.09

with different values of  $n$  and  $s$  are given in Table 2. A comparison between the different  $K_{1ns}$  values directly shows the Cd<sup>2+</sup> ion to be a stronger complexing agent for Cl<sup>-</sup> than the binary CdL<sub>*n*</sub><sup>2+</sup> as well as the ternary CdL<sub>*n*</sub>Cl<sub>*s*</sub> complexes. However, it can be noted that for the reaction



$\log K (n=0)=0.80$  and  $\log K (n=1)=0.78$ , thus almost the same values. The high stability of this ternary complex is most probably due to a coordination shift leading to a tetrahedral configuration as in CdCl<sub>3</sub><sup>-</sup>.

A decreased stability of the ternary complexes in comparison with the binary CdCl<sub>2-3</sub> species has also been found in other ternary Cd<sup>2+</sup>-L-X<sup>-</sup> systems, where L stands for organic ligands such as thiourea,<sup>15</sup> glycine,<sup>16</sup> ethylenediamine,<sup>16</sup> the inorganic ligand sulfate<sup>17</sup> and X<sup>-</sup> stands for the halides Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>.

To determine whether there is any mutual influence between imidazole and Cl<sup>-</sup> in the ternary complexes or if statistical reasons alone determine their formation, statistical equilibrium constants  $\beta_{ns}$  (Cd<sup>2+</sup>+*n*L+*s*Cl<sup>-</sup> ⇌ CdL<sub>*n*</sub>Cl<sub>*s*</sub><sup>(2-s)+</sup>) have been calculated according to the formula<sup>17</sup>

$$\log \beta_{ns} = \frac{n \log \beta_{N0+s} \log \beta_{0N}}{N} + \log \frac{N!}{n!s!}$$

where  $N=n+s$ .

Table 4. Some stepwise reactions for the Zn group by means of formation constants given in Ref. 2, this paper and Ref. 3, and proposed configuration. The different reactions define the stepwise uptake of the ligands Cl<sup>-</sup>, C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>(L) are to be read horizontally.

ex. MeCl <sup>+</sup>	3.64 (o)	MeLCl <sup>+</sup> stands for	ZnCl <sup>+</sup> +L ⇌ ZnLCl <sup>+</sup>	log K=3.64
	2.60 (o)		CdCl <sup>+</sup> +L ⇌ CdLCl <sup>+</sup>	log K=2.60
	9.18 (l)		HgCl <sup>+</sup> +L ⇌ HgLCl <sup>+</sup>	log K=9.18

(o), (t) and (l) stand for octahedral, tetrahedral and linear coordination, respectively.

MeCl <sub>3</sub> <sup>-</sup>	-0.15(t) 1.07(t)	MeCl <sub>4</sub> <sup>2-</sup>			
MeCl <sub>2</sub>	0.75(t) 0.15(t) 1.07(t)	MeCl <sub>3</sub> <sup>-</sup>	3.45(t) 2.77(t) 3.08(t)	MeLCl <sub>3</sub> <sup>-</sup>	
MeCl <sup>+</sup>	0.41(t) 0.65(o) 6.78(l)	MeCl <sub>2</sub>	- - 3.15(t)	MeLCl <sub>2</sub>	7.53 <sup>a</sup> (t) 4.38 <sup>a</sup> (o) 6.23 <sup>a</sup> (t)
Me <sup>2+</sup>	0.19(o) 1.55(o) 7.22(l)	MeCl <sup>+</sup>	3.64(o) 2.60(o) 9.18(l)	MeLCl <sup>+</sup>	2.52(o,t)? 1.93(o) 2.48(t)
		Me <sup>2+</sup>	2.93(o) 3.09(o) 9.18(l)	MeL <sup>2+</sup>	2.00(t) 2.41(o) 9.01(l)
				MeL <sub>2</sub> <sup>2+</sup>	3.61(t) 1.69(o) -
				MeL <sub>3</sub> Cl <sup>+</sup>	-
				MeL <sub>2</sub> <sup>2+</sup>	3.79(t) 1.79(o) -
				MeL <sub>3</sub> <sup>2+</sup>	2.82(t) 1.22(o) -
				MeL <sub>4</sub> <sup>2+</sup>	-

<sup>a</sup> The formation constants given include the uptake of two ligands (MeCl<sub>2</sub>+2L ⇌ MeL<sub>2</sub>Cl<sub>2</sub>).

By using proposed formation constants for  $\text{CdL}_n^{2+}$ ,  $n=2, 3, 4$  and  $\text{CdCl}_s^{(2-s)+}$ ,  $s=2, 3, 4$  and assuming that  $\log \beta_{\text{CdCl}_4^{2-}}=2.2$ <sup>5,17</sup> it is possible to calculate statistical values for all ternary complexes found in this system. The result is given in Table 3.

It can be seen from this table that the two- and three-coordinated complexes  $\text{CdLCl}^+$  and  $\text{CdL}_2\text{Cl}^+$  are formed by statistical reasons, while the four-coordinated complexes  $\text{CdL}_3\text{Cl}^+$ ,  $\text{CdL}_2\text{Cl}_2$  and  $\text{CdLCl}_3^-$  are significantly stronger than predicted from statistical reasoning. Thus the formation of four-coordinated complexes are determined by entropy as well as enthalpy changes.

It is interesting to note that similar behaviour is found for the ternary complexes  $\text{HgLCl}^+$  and  $\text{HgOHCl}^+$  which are formed by statistical reasons, while  $\text{Zn}^{2+}$  forms ternary complexes with imidazole and chloride which are considerably stronger than are predicted from statistical values.

*Stabilities of Zn, Cd, Hg complexes.* By means of the results obtained in this investigation, it has become possible to compare stabilities of different binary and ternary complexes with the ligands imidazole and chloride in the 2B group (Zn, Cd, Hg). Complexation in the corresponding  $\text{Zn}^{2+}$  (Forsling) and  $\text{Hg}^{2+}$  system (Sjöberg)<sup>3</sup> has earlier been studied under similar experimental conditions.

It is well-known that Zn and Cd usually form complexes with octahedral or tetrahedral configuration. Mercury, on the other hand, shows a preference for linear and tetrahedral coordination.

In the  $\text{Zn}^{2+}$ -imidazole- $\text{Cl}^-$  system coordination shifts seem to occur frequently. Besides a shift at the second step in the  $\text{ZnCl}_s^{2-s}$  series, octa- and tetrahedral complexes are formed in the binary  $\text{ZnL}_n^{2+}$  series as well as among the ternary  $\text{Zn}^{2+}$ -L- $\text{Cl}^-$  species.

In the  $\text{Hg}^{2+}$  system the most stable species are linear, and three- and four-coordinated complexes have much lower stability.

In the present system, the validity of the 2-parameter approximation within the  $\text{CdL}_n^{2+}$  series indicates no coordination shift. These complexes are most probably octahedral, as has been shown for  $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ <sup>18</sup> and  $\text{CdL}_6^{2+}$ <sup>1</sup> from structural investigations. Octahedral configuration has also been found in the solid phases

$(\text{CdLCl}_2)_n$ <sup>13</sup> and  $(\text{CdL}_2\text{Cl}_2)_n$ <sup>14</sup> and it seems likely that the corresponding mononuclear complexes in aqueous solution have a similar coordination. From NMR<sup>19</sup> and calorimetric<sup>20</sup> measurements, tetrahedral configuration in  $\text{CdCl}_3^-$  and  $\text{CdCl}_4^{2-}$  has been proposed.

A review of the stabilities of the different species formed in the 2B group is given in Table 4. Most probable configuration of the complexes are also indicated. As can be seen, it is possible to compare stabilities of different types of complexes (tetrahedral (t), octahedral (o) and linear (l)) within this group. For tetrahedral binary and ternary chloro complexes, e.g.  $\text{MeCl}_3^-$  and  $\text{MeLCl}_3^-$ , the stability seems to increase within the series:



Irrespective of type of configuration all ternary complexes show the same trend in stability, i.e.  $\text{Zn} > \text{Cd} < \text{Hg}$ . For the different imidazole complexes, the tetrahedral Zn species are more stable than the corresponding octahedral Cd species.

*Acknowledgements.* We wish to thank Professor Nils Ingri for his great interest and for all the facilities placed at our disposal. The English of the present paper has been corrected by Dr. Michael Sharp. The work forms part of a program financially supported by the Swedish Natural Science Research Council.

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Received October 8, 1982.