

## Cadmium-Imidazole Complex Formation in Aqueous Solutions. Preparation and Characterization of Compounds with Five and Six Ligands

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The fifth and sixth complex compound between cadmium and imidazole have been isolated and characterized. The counterions were perchlorate and nitrate, respectively. With chloride as counterion in the corresponding complex compound the Cd-ion probably enters the crystal lattice in an oxidation state lower than 2.

The formulas of the fifth and sixth complex compound were found to be  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  and  $\text{Cd im}_6(\text{NO}_3)_2$ , respectively (im = imidazole). Concerning the complex compound with chloride as counterion the formula  $\text{Cd}_4^{\text{II}}(\text{Cd}_2^{\text{I}})\text{im}_{28}\text{Cl}_{10}$  is suggested.

Reactions in which divalent Cd-ions may undergo reductions to a lower oxidation state than 2 are discussed.

From analysis of the polarographic results from the cadmium-imidazole system and estimation of activity coefficients of imidazole it was shown in a previous paper<sup>1</sup> that the maximum coordination number of the Cd-ion against imidazole was 6.

In order to support the results from the polarographic studies our efforts have been directed towards the preparation of complex compounds with five and six imidazole ligands per cadmium ion by suitable synthetic methods. To our knowledge none of these compounds have previously been isolated.

Earlier it was reported<sup>2</sup> that  $\text{Cd}^{2+}$ -ethylenediamine complexes form slightly soluble perchlorates and nitrates. Therefore our experiments have been concentrated mainly on these two ions. In addition, some experiments have been carried out with chloride.

## EXPERIMENTAL

*Preparations.* According to Leden<sup>3</sup>  $\text{Cd}(\text{ClO}_4)_2$  was prepared by dissolving  $\text{CdCO}_3$  in  $\text{HClO}_4$ . The crude product was recrystallized by dissolving in hot water and cooling in an ice bath. The Cd-content was controlled by potentiometric titrations. All other chemicals mentioned below were of reagent grade and were used without further purification. The temperature was kept constant at  $25 \pm 0.1^\circ\text{C}$  by means of a thermostated water-bath.

1. The perchlorate precipitate was prepared by dissolving 0.5 mol imidazole into 1 liter well-stirred 1.0 M  $\text{NaClO}_4$ . pH was adjusted to 9.5 by addition of  $\text{HClO}_4$  using a glass electrode. To this solution, 1 ml 1.0 M  $\text{Cd}(\text{ClO}_4)_2$  was added. Immediately a white, voluminous precipitate was formed. This precipitate was isolated by filtration, quickly washed with cooled ethanol and dried in vacuum. (Found: Cd  $17.0 \pm 0.2$ ; im  $51.5 \pm 0.5$ ;  $\text{ClO}_4$   $29.4 \pm 1$ . Calc. for Cd im<sub>5</sub>aq ( $\text{ClO}_4$ )<sub>2</sub>: Cd 16.8; im 50.8;  $\text{ClO}_4$  29.7). The term im is used as an abbreviation for the unprotonated imidazole molecule.

2. The nitrate precipitate was prepared by dissolving 0.5 mol imidazole into 1 liter well-stirred 1.0 M  $\text{NaNO}_3$  and adjusting the pH to 9.5 by adding  $\text{HNO}_3$ . 10 ml 1.0 M  $\text{Cd}(\text{NO}_3)_2$  was added. After stirring for about 10–15 min, a crystalline precipitate appeared. The precipitate was isolated by filtration, washed with ethanol and dried in vacuum. (Found: Cd  $17.2 \pm 0.2$ ; im  $64.0 \pm 0.5$ ;  $\text{NO}_3$   $19.4 \pm 0.5$ . Calc. for Cd im<sub>6</sub>( $\text{NO}_3$ )<sub>2</sub>: Cd 17.4; im 63.3;  $\text{NO}_3$  19.2).

3. In a stirred solution of 1 liter 0.5 M imidazole at an ionic strength 1.0 established with KCl, the pH was adjusted to 9.5 by addition of HCl. Finally, 10 ml 1.0 M  $\text{CdCl}_2$  was added. The solution was left unstirred and undisturbed, and after 1 or 2 d the crystallization was gradually initiated yielding pale white, almost colourless crystals. The crystallization continued for several days. The crystals were isolated, washed with ethanol and dried in vacuum. (Found: Cd  $23.0 \pm 0.2$ ; im  $65.5 \pm 0.5$ ; Cl  $12.0 \pm 0.1$ . Calc. for  $\text{Cd}_4^{\text{II}}(\text{Cd}_2^{\text{I}})\text{im}_{28}\text{Cl}_{10}$ : Cd 23.0; im 65.0; Cl 12.0).

*Analysis and measurements.* The imidazole analyses were performed on an automatic titration equipment (SBR2, PHM26, TTT11, ABU1, TTA3, Radiometer, Copenhagen, Denmark). The pH was initially adjusted to 3.00 using  $\text{HClO}_4$ ,  $\text{HNO}_3$ , and HCl, respectively, and the imidazole content was determined from difference titration curves, *i.e.* the difference between titration curves for complex compounds and acids. To avoid precipitation of  $\text{Cd}(\text{OH})_2$  the titrations were terminated at approximately pH 9.5. In addition some titrations were carried out on solutions from which the  $\text{Cd}^{2+}$ -ions had beforehand been removed with  $\text{Na}_2\text{S}$ .

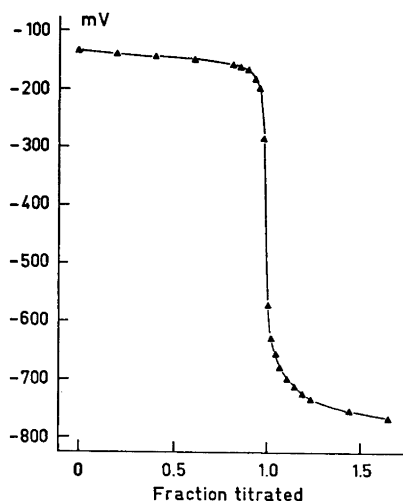


Fig. 1.  $\text{Na}_2\text{S}$  titrations of  $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$  using  $\text{Ag}/\text{Ag}_2\text{S}$  as indicator electrode and  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4(\text{s})$  as reference electrode. The mV-values are converted to values relative to a saturated calomel electrode.

The chloride analyses were carried out by potentiometric titration using Ag/AgCl and Hg/Hg<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>(s) electrodes. Likewise, the cadmium analyses were carried out potentiometrically, using the method described by Hiltner and Grundmann.<sup>4</sup> The Ag/Ag<sub>2</sub>S electrode was prepared from a silver pellet electrode (Radiometer P4011) on which Ag<sub>2</sub>S was deposited by electrolysis. By means of this electrode the cadmium ions could be determined very precisely by potentiometric titrations<sup>4</sup> using a Hg/Hg<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>(s) electrode as reference electrode. Duplicate experiments showed that it was possible to determine the cadmium content with a reproducibility of about 0.5 %. A titration curve is shown in Fig. 1. The potentials are converted to values relative to a saturated calomel electrode. Regarding the Ag/Ag<sub>2</sub>S electrode as a second order electrode, the electrode potential can be calculated from the Nernst-equation:

$$(\pi - \psi) = \pi^0 - 29.56 \log a_{S^{2-}} \quad (25^\circ\text{C})$$

where  $(\pi - \psi)$  indicated the electrode potential, expressed in mV,  $\pi^0$  the oxidation potential at  $a_{S^{2-}} = 1$ , and  $a_{S^{2-}}$  the activity of sulphide ion. According to Latimer<sup>5</sup>  $\pi^0$  has the value  $-690$  mV *vs.* normal hydrogen electrode at ionic strength = 0. At the equivalence point  $a_{S^{2-}} = a_{Cd^{2+}} = (L_{CdS})^{\frac{1}{2}}$  where  $L_{CdS}$  is the solubility product of CdS. Using this information the potential at the equivalence point of the titration curve was calculated to approx.  $-475$  mV *vs.* saturated calomel electrode in good agreement with the experimental results shown in Fig. 1. The freezing point measurements were carried out on a Fiske osmometer (Fiske Associates, Inc., Uxbridge, Mass. USA), and vapour pressure measurements on a Knauer osmometer (H. Knauer & Co., GmbH, Berlin, BRD). The DTA measurements were carried out on a DTA-equipment from Bureau de Liaison, Paris. The absorbance spectra were obtained on a Beckmann DB spectrophotometer. Nitrate and perchlorate analyses were performed using nitron as described by Busch.<sup>6</sup>

## RESULTS AND DISCUSSION

The complex compound from the perchlorate solution, here abbreviated as Cd-im-ClO<sub>4</sub>, crystallizes easily in white very voluminous threads almost like cotton. In all probability the crystals can be classed within the monoclinic crystal group. The solubility of Cd-im-ClO<sub>4</sub> is strongly dependent on temperature. This gave us a convenient way to determine its solubility product. A solution containing  $5 \times 10^{-4}$  M Cd(ClO<sub>4</sub>)<sub>2</sub>, 1.0 M NaClO<sub>4</sub>, and 0.5 M imidazole at pH = 9.5 and 25°C is just saturated and without precipitate. When lowering the temperature to 23°C white crystals of Cd-im-ClO<sub>4</sub> are formed. However, they redissolve when the temperature is raised to 25°C. Earlier<sup>1</sup> it was shown that in a solution of the above mentioned composition only about 24 % of the cadmium ions are in the Cd im<sub>5</sub>aq<sup>2+</sup> form. Since the experiments were carried out in a 1.0 M NaClO<sub>4</sub> solution it may be assumed that the activity coefficients of all the ions present in the solution are determined by the NaClO<sub>4</sub>. Assuming that  $\log \gamma_{Cd \text{ im}_5\text{aq}(\text{ClO}_4)_2} = 3 \log \gamma_{\text{NaClO}_4}$  is valid in the present solution we are able to calculate the solubility product by means of tabulated values for  $\gamma_{\text{NaClO}_4}$  from Robinson and Stokes<sup>7</sup>

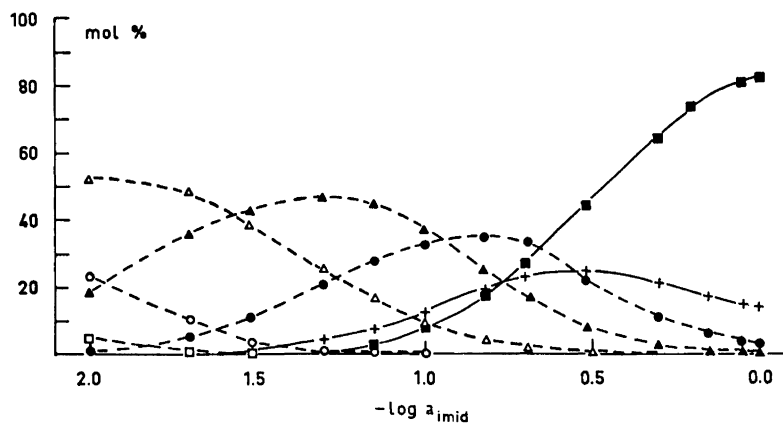
$$L_{sp} = c_{Cd \text{ im}_5\text{aq}^{2+}} c_{\text{ClO}_4^{2-}}^2 \gamma_{\text{NaClO}_4}^3 = \text{approx. } 2 \times 10^{-5} \text{ mol}^3/\text{l}^3$$

This is in good agreement with the results shown in Table 1 where the solubility of the Cd-im-ClO<sub>4</sub> in 0.1 M HClO<sub>4</sub> is tabulated together with the solubilities of the NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> complex compounds in 0.1 M of their corresponding acids, *i.e.* 0.1 M HNO<sub>3</sub> and 0.1 M HCl, respectively, to prevent precipitation of Cd(OH)<sub>2</sub>.

*Table 1.* The solubilities of the investigated cadmium imidazole complex compounds in 0.1 M of their corresponding acids.  $t=25^{\circ}\text{C}$ . + indicates formation of precipitates, - indicates no precipitate.

Concentration of complex compounds mol/l	Counterion (in brackets the corresponding acid)		
	$\text{ClO}_4^- (\text{HClO}_4)$	$\text{Cl}^- (\text{HCl})$	$\text{NO}_3^- (\text{HNO}_3)$
0.05	-	- (+) very little precipitate formed	-
0.1	+	+	-
0.2	++	++	+

In Fig. 2 is shown the mol percentage of individual cadmium-imidazole complexes as a function of log of imidazole activity at ionic strength 1.0 with sodium perchlorate. From this figure it appears that the fifth complex compound has its maximum value at  $C_{\text{imid}} \cong 4.0 \times 10^{-1} \text{ M}$  ( $a_{\text{imid}} \cong 3.5 \times 10^{-1} \text{ M}$ ). In



*Fig. 2.* Percentage of individual cadmium-imidazole complexes as a function of log of imidazole activity. Ionic strength = 1.0 with sodium perchlorate. Total Cd-contents =  $5 \times 10^{-4} \text{ M}$ , pH = 9.5,  $t = 25^{\circ}\text{C}$ . Only the last two curves are fully drawn up. For details: see text. Explanation of symbols:  $\square$   $\text{Cd aq}_6^{2+}$ ,  $\circ$   $\text{Cd imaq}_5^{2+}$ ,  $\triangle$   $\text{Cd im}_2\text{aq}_4^{2+}$ ,  $\blacktriangle$   $\text{Cd im}_3\text{aq}_3^{2+}$ ,  $\bullet$   $\text{Cd im}_4\text{aq}_2^{2+}$ ,  $+$   $\text{Cd im}_5\text{aq}^{2+}$ ,  $\blacksquare$   $\text{Cd im}_6^{2+}$ .

other words when more imidazole is added to a solution of 0.4 M imidazole with a small precipitate of  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  it must be expected that precipitate would redissolve due to the reaction  $\text{Cd im}_5\text{aq}^{2+} + \text{im} \rightarrow \text{Cd im}_6^{2+} + \text{aq}$ , *i.e.* the solubility product of  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  is no longer exceeded. This is actually what happens: In a solution of 0.1 M imidazole,  $1.0 \times 10^{-3} \text{ M}$   $\text{Cd}(\text{ClO}_4)_2$ , and 1.0 M  $\text{NaClO}_4$  at  $25^{\circ}\text{C}$  and pH = 9.5 no precipitate is found. When more imidazole is added stepwise, the precipitation starts at 0.2 M, the maximum value

being reached at 0.4 M. At a concentration of imidazole of 1.0 M the precipitate has dissolved again. The fact that the formation curve in Fig. 2 may be reconstructed in this way supports the result from the analyses and makes it very likely that the precipitate has the postulated composition,  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  a postulate which is further supported by freezing point and vapour pressure measurements.

Fig. 3 shows the results from the freezing point measurements. Curve B represents the points measured directly, and in curve A the points are cor-

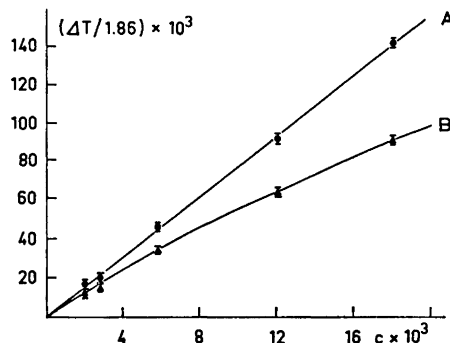
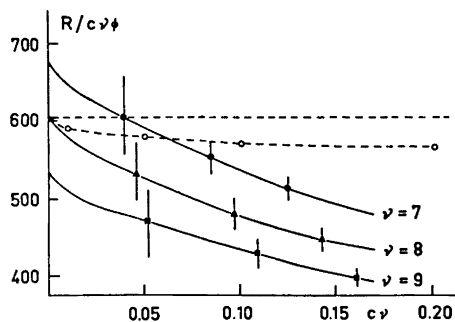


Fig. 3. Dependence of the freezing point depression of the perchlorate complex on the concentration of this complex. Curve B: measured values. Curve A: The measured values corrected for complex formation by which a straight line is formed. The slope of this line has the value 7.85 indicating the formula  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  for the complex compound.

rected for complex formation by means of which a straight line is formed. The slope of this line has the value 7.85 indicating that the most likely number of dissociated particles from the investigated compound is 8 in agreement with the previously mentioned composition. The results from vapour pressure

Fig. 4. Vapour pressure measurements on the perchlorate complex. The dotted line with open circles represents values from measurements on sodium chloride solutions. The horizontal dotted line represents the same values corrected for osmotic coefficients. The condition that all the curves must coincide at infinite dilution is seen to be fulfilled only when  $\nu$  is given the value 8, corresponding to the formula  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  for the perchlorate complex. The letter R on the ordinate axis indicates the measured value in arbitrary units.



measurements are represented in Fig. 4. The calibration curve based on measurements on NaCl is shown as dotted lines. When extrapolated to infinite dilution the curves must coincide at a point on the ordinate axis determined by the NaCl curve. This condition can only be fulfilled when  $\nu$  is given the value 8.

Care must be taken when  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  is prepared to avoid precipitation of complex compound coordinated with six im-molecules, *i.e.*  $\text{Cd im}_6(\text{ClO}_4)_2$ . From Fig. 2 it appears that in a solution of 1.0 M imidazole, 1.0 M  $\text{NaClO}_4$ , and  $5 \times 10^{-4}$  M  $\text{Cd}(\text{ClO}_4)_2$  at  $\text{pH} = 9.5$  the larger part of the cadmium ions is coordinated with six im, whereas only a small amount has five im. In this solution, no precipitation was observed at 25°C. When adding more  $\text{Cd}(\text{ClO}_4)_2$  to a well-stirred solution of this composition white crystals are formed at once. When analyzed in the normal way the precipitate turns out to be an inhomogeneous mixture of the fifth and sixth complex compound. In other words by this procedure the solubility product is exceeded for the perchlorates of both of the two complexes.

Results from solubility experiments in organic solvents showed that  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  is very soluble in both ethanol and acetone but almost insoluble in ether. The heat stability has been examined by DTA measurements. The temperature was increased from 25°C to 130°C. According to the results from these experiments  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  is stable up to 110°C. At 120°C a weak exothermic reaction occurs, probably caused by decomposition. Analyses (of  $\text{Cd}^{2+}$ , im, and  $\text{ClO}_4^-$ ) on crystals, which were kept at 100°C for 24 h, and on vacuum dried crystals, gave identical results.

*The complex compound from the nitrate solution* forms trigonal, optically active, almost colourless crystals built as parallelepipedons. According to the results from analyses the crystals were identified as the six-coordinated complex compounds, *i.e.*  $\text{Cd im}_6(\text{NO}_3)_2$ , and only this compound was found in the precipitate from the nitrate solutions. This indicates greater solubility of  $\text{Cd im}_5\text{aq}(\text{NO}_3)_2$  compared with  $\text{Cd im}_6(\text{NO}_3)_2$  contrary to what was the case in perchlorate solutions. Consequently, in nitrate solutions, more crystals are formed when more imidazole is added, contrary to what happened in perchlorate solutions where the almost insoluble  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  in this way was converted to the more soluble  $\text{Cd im}_6(\text{ClO}_4)_2$  and the crystals disappeared.

The solubility of  $\text{Cd im}_6(\text{NO}_3)_2$  is strongly temperature dependent, just as that of the perchlorate complex, and the solubility product could therefore be determined by the same method. The solubility product was calculated to

$$L_{\text{sp}} = c_{\text{Cd im}_6^{2+}} c_{\text{NO}_3^-}^2 \gamma_{\text{NaNO}_3}^3 \cong 4 \times 10^{-4} \text{ mol}^3/\text{l}^3$$

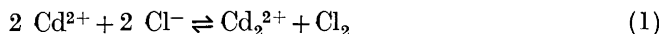
Table 1 summarizes the solubilities of  $\text{Cd im}_6(\text{NO}_3)_2$  in 0.1 M  $\text{HNO}_3$ . Results from solubility experiments in organic solvents showed that  $\text{Cd im}_6(\text{NO}_3)_2$  is very soluble in ethanol but almost insoluble in acetone and ether.

The DTA measurements showed that  $\text{Cd im}_6(\text{NO}_3)_2$  was stable up to a temperature of 80°C where a weak endothermic reaction occurred and the compound got an amorphous plastic-like consistency. At approximately 100°C the colour changed from white to yellow. All the crystals were lost and a yellow liquid was formed. When cooled no crystals were reformed whereas the result was an amorphous glass-like solid.

*The complex compound from the chloride solutions* form crystals which most probably can be classed within the hexagonal crystal group. According to results from analyses the only way to explain the electroneutrality for the crystals is to assume that cadmium is present in the crystal partly as ions in a lower oxidation state than 2.

The existence of the monovalent cadmium ion is established in the literature.<sup>5</sup> Grantham<sup>8</sup> demonstrated that the cadmium dimer ion  $\text{Cd}_2^{2+}$  is extremely stable in Cd-CdCl<sub>2</sub> melts at temperatures near the freezing point of the salt. Very recently<sup>9,10</sup> it has been suggested that when cadmium and zinc are electrolytically dissolved in alkaline solutions, monovalent ions are found in both cases. In accordance with this, the composition of the precipitate formed in the system containing 0.01 M CdCl<sub>2</sub>, 0.5 M imidazole, and 1.0 M KCl at pH=9.5 is assumed to have the formula  $\text{Cd}_4^{II}(\text{Cd}_2^I)\text{im}_{28}\text{Cl}_{10}$ . This assumption is based partly on the results from experiments carried out in this laboratory, partly on the above mentioned investigations.

1. Before the cadmium ion is able to enter the crystal lattice as monovalent ion it must undergo a reduction and, of course, simultaneously another component must be oxidized. Imidazole is known<sup>11</sup> to be very stable to oxidizing agents, and so it is only possible to create monovalent cadmium ions in solutions where the anions can be oxidized. With Cl<sup>-</sup> as anion the redox process is supposed to be:



Neither NO<sub>3</sub><sup>-</sup> nor ClO<sub>4</sub><sup>-</sup> are able to take part in a redox process similar to (1) and consequently  $\text{Cd}_2^{2+}$  cannot be found in these solutions. The chlorine formed according to reaction (1) will not be identified as free Cl<sub>2</sub>. According to Albert<sup>11</sup> halogenation of imidazole in alkaline solutions is very brisk, *i.e.* if the reaction (1) takes place we would expect to find the chlorine bound to imidazole.

Since it might be expected that the absorbance spectrum from this chlorinated imidazole molecule is different from that of the free imidazole, an attempt was made to identify this compound by means of spectrophotometric measurements. In Fig. 5 is shown the UV absorbance spectra from these experiments. No difference in the absorbance spectra was observed in the visible region. Curve A shows the absorbance spectrum of 0.5 M chlorinated imidazole in 1.0 M KCl, prepared in this institute, in 1.0 M KCl, pH=9.5. Curve B shows the absorbance spectrum of 0.5 M pure imidazole in 1.0 M KCl, pH=9.5. In both

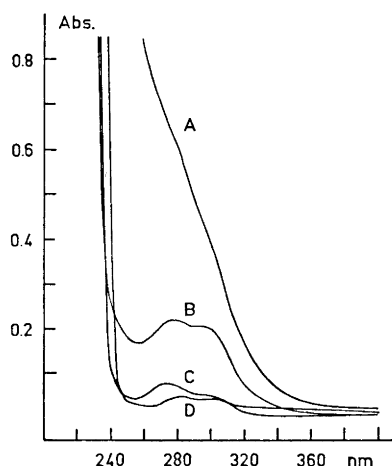


Fig. 5. Absorbance spectra of curve A: 0.5 M chlorinated imidazole in 1.0 M KCl, curve B: 0.5 M imidazole in 1.0 M KCl. Reference solution for A and B: 1.0 M KCl. Curve C: Filtrate from the KCl solution in which the complex compound was precipitated, curve D: 0.5 M imidazole in 1.0 M KCl. Reference solution for C and D: 0.495 M imidazole in 1.0 M KCl. In all solutions pH was 9.5.

curve A and B the reference solution was 1.0 M KCl,  $\text{pH} \approx 9.5$ . The solution containing the complex compound as precipitate was filtered through a glass filter, and the filtrate was used in the spectrophotometric measurements. The result appears in curve C. Curve D belongs to pure 0.5 M imidazole in 1.0 M KCl,  $\text{pH} = 9.5$ . Reference solution in case C and D was solution D diluted with 1% KCl in order to obtain the same concentration of imidazole in solution C and D. Since the difference between the curves C and D is greatest at approx. 270 nm, where also the difference between the curves A and B is very great, the assumption can be made that the solution in which the complex precipitate is formed most likely also contains the chlorinated imidazole compound and consequently Cd-ions in a lower oxidation state than 2 according to eqn. (1).

2. When the crystals formed from complex formation were dissolved in hydrochloric acid, a gas evolution was observed. As suggested by Latimer<sup>8</sup> the gas evolution can be explained by the following reaction:



This reaction – or a reaction similar to it – also explains why the cadmium ions, when titrated with sodium sulphide, always react as divalent Cd-ions. This appears from titration curves, which indicate only one point of equivalence together with the fact that the total amount of  $\text{Cd}^{2+}$ , imidazole, and  $\text{Cl}^-$  determined as earlier mentioned yields within the experimental error 100 %. If the Cd-ions should exist in the crystals solely as divalent ions, then the mol ratio between Cl and Cd-ions should be 2:1 in order to fulfill the condition of electroneutrality. Experimentally, we found the ratio 1.67:1, indicating that the cadmium ions are present in the crystal in lower valency than two, possibly as the dimer  $\text{Cd}_2^{2+}$  as suggested by Grantham.<sup>8</sup> Reaction (2) can also be observed titrimetrically. A difference in base consumption when two specific amounts of hydrochloric acid with and without complex compound are titrated with sodium hydroxide, indicates that some cadmium ions are oxidized and free hydrogen is formed. The results from four such experiments showed that  $40 \pm 5$  % of the Cd-ions were oxidized according to (2).

These experiments involved some uncertainty mainly due to trouble in connection with exclusion of air, but the effect was very clear: less base consumption for titration of hydrochloric acid in the case where the complex compound was dissolved in the acid, in full agreement with reaction (2). At the present time more experiments are prepared in this institute to support the assumption of monovalent Cd-ions. The results from these experiments will be discussed elsewhere but on the basis of the present experiments it seems possible to assume that the Cd-ions exist in the crystal probably in the dimer form  $\text{Cd}^+ - \text{Cd}^+$  similar to the mercurio ions, and so we here propose the formula:  $\text{Cd}_4^{\text{II}}(\text{Cd}_2^{\text{I}})\text{im}_{28}\text{Cl}_{10}$ . In the DTA measurements the temperature was increased continuously from 25°C to 100°C. From these experiments it appeared that no heat involving reactions occurred within these limits of temperature. The results from the solubility experiments in 0.1 M HCl are summarized in Table I. Results from solubility experiments in organic solvents showed that  $\text{Cd}_4^{\text{II}}(\text{Cd}_2^{\text{I}})\text{im}_{28}\text{Cl}_{10}$  is almost insoluble in ethanol, acetone, and ether. Just like in the case of  $\text{Cd im}_5\text{aq}(\text{ClO}_4)_2$  and  $\text{Cd im}_6(\text{NO}_3)_2$  the solubility



of the complex compound with  $\text{Cl}^-$  as counterion was found to be strongly temperature dependent. Using this information we found the solubility at  $25^\circ\text{C}$  to be approximately  $5 \times 10^{-2}$  mol  $\text{Cd}_4^{\text{II}}(\text{Cd}_2^{\text{I}})\text{im}_{28}\text{Cl}_{10}$  per litre.

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## REFERENCES

1. Jensen, J. B. *Acta Chem. Scand.* **26** (1972) 4031.
2. Glöckner, W. *Die Komplexverbindungen*, Aulis Verlag Deubner & Co., KG., Köln, BRD, 1962.
3. Leden, I. *Potentiometrisk undersökning af några kadmiumsalters komplexitet*, Glerupska Univ. Bokhandeln, Lund 1943.
4. Hiltner, W. and Grundmann, W. *Z. physik. Chem.* **168** (1933) 291.
5. Latimer, W. M. *The oxidation states of the elements and their potentials in aqueous solutions*, 2nd Ed., Prentice-Hall, Englewood Cliffs, New Jersey 1952.
6. Busch, M. *Ber.* **38** (1905) 861.
7. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1955.
8. Grantham, L. F. *J. Chem. Phys.* **44** (1966) 1509.
9. Bockris, J. O. M., Nagy, Z. and Damjanovic, A. *J. Electrochem. Soc.* **119** (1972) 285.
10. Azin, A. A. A. and El-Sobki, K. M. *Electrochim. Acta* **17** (1972) 601.
11. Albert, A. *Heterocyclic Chemistry*, 2nd Ed., The Athlone Press, London 1968.

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