

POLAROGRAPHIC STUDY  
OF THE SUBSTITUTION REACTIONS OF THE CHELATES  
OF TRIETHYLENETETRAMINEHEXAACETIC ACID. II.\*

REACTIONS OF THE CHELATES  
OF TRANSITION METALS

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Electrophilic substitution reactions of the chelates of triethylenetetraminehexaacetic acid (TTHA,  $H_6X$ ) were studied using polarographic technique. It has been found that relatively stable mixed binuclear chelates of the type  $CdMeX^{2-}$  were formed in the reaction of cadmium triethylenetetraminehexaacetate with nickel(II) or zinc(II) or cobalt(II) or copper(II) ions. Stability constants of mixed binuclear chelates were calculated using data obtained by polarographic measurements in the system studied;  $\log K_{CdNiX}^{Cd} = 9.2$ ;  $\log K_{ZnNiX}^{Zn} = 13.8$  and  $\log K_{CdZnX}^{Zn} = 12.6$ . Validity of the experimental technique and the treatment of the obtained data was verified by the determination of the stability constants of the Cd-TTHA (1 : 1) and Zn-TTHA (2 : 1) chelates determined previously by potentiometric method.

In the paper<sup>1</sup> the mechanism of the substitution reaction between zinc triethylenetetraminehexaacetate and calcium ions has been studied and the existence of the binuclear mixed chelate was verified. The present paper presents the results of a study involving the reactions of the triethylenetetraminehexaacetic acid (TTHA,  $H_6X$ ) chelates of some transition metals. Obtained results have shown that the existence of binuclear mixed chelates is a common phenomenon occurring in the system containing the TTHA reagent and two metals ions. Polarographic method was applied for the determination of the equilibrium concentration of the reacting components.

## EXPERIMENTAL

### Reagents and Apparatus

All the used solutions were prepared from reagent-grade chemicals. The metal salt solutions were standardized by visual amperometric titrations with EDTA reagent using the recommended proce-

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dures. TTHA solution (0.01 mol/l) was prepared from the reagent of Geigy Chemical Co., Basel, Switzerland, and standardized by visual titration with standard zinc solution<sup>2</sup>.

Polarographic measurements were performed with a Polarecord, Metrohm E 261 R and with polarograph PO 4 Radiometer. The H type polarographic cell with a separate saturated calomel electrode was used. The temperature was kept constant at 22°C. Neutralization titrations were carried out potentiometrically using the pH meter PHM 22, Radiometer and glass electrode.

### Procedure

Polarographic measurements in systems containing two metal ions M and N and the TTHA reagent were carried out in three ways.

1. The mixture of the both metal ions was titrated with the reagent and the course of the resulting titration curve was indicated polarographically (after each addition of the reagent the polarogram was recorded). 2. The time dependence was estimated of the amount of M ions released from the MX chelate by the action of the ion N. (A given amount of N ions was added to the solution containing MX chelate and the concentration of released M ions and nonchelated N ions was measured polarographically). 3. The dependence of the concentration of M ions, released from the MX chelate, on the stepwise increased concentration of the ions N was determined polarographically. With respect to the previously determined time dependence, these measurements were carried out at the proper time after mixing of all components.

Some additional measurements, the potentiometric neutralization of the reagent and of the mixture reagent + metal ion were carried out as proposed by Schwarzenbach<sup>3</sup>.

To calculate the equilibrium data, total concentration of ammonia  $C_{\text{NH}_3}$  was always used instead of the equilibrium concentration  $\text{NH}_3$ . This approximation was done because in all cases total concentration of ammonia was very high compared with the concentration of metal ions or the reagent. Concentration of  $\text{NH}_4^+$  ion was also neglected, because at pH about 11 and in the concentration range of ammonia 0.5–1.0 mol/l the concentration of  $\text{NH}_4^+$  ions is lower than  $C_{\text{NH}_3}$  (approx. one order).

## RESULTS AND DISCUSSION

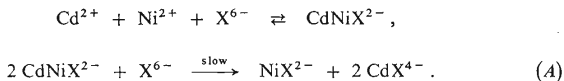
### SYSTEM CONTAINING CADMIUM(II) AND NICKEL(II) IONS AND TTHA REAGENT

#### *Preliminary Experiments*

Preliminary experiments carried out with the system containing nickel(II) and cadmium(II) ions and TTHA reagent in ammoniacal medium have shown the time dependence of the reaction between both metal ions and the reagent. Amperometric titration of cadmium(II) ions with TTHA carried out in ammoniacal medium have indicated the formation of 2 : 1 and 1 : 1 metal to ligand chelates. Because both these chelates are polarographically inactive<sup>4</sup> the course of the amperometric titration curve (limiting current of nonchelated cadmium ions *vs.* the amount of added reagent, Fig. 1, curve 1) may be interpreted as follows: At the beginning of the titration the prevailing species formed are the  $\text{Cd}_2\text{X}^{2-}$  and further the excess of the reagent enables the formation of the 1 : 1 cadmium chelate. When such titration was carried out visually, using a suitable metallochromic indicator, only the formation of 2 : 1

chelate was observed<sup>2</sup>. The amperometric titration of nickel(II) ions with TTHA reagent carried out under identical conditions showed only the formation of  $\text{Ni}_2\text{X}^{2-}$  chelate. (Fig. 1, curve 2). Also in this case the nickel chelate is polarographically inactive<sup>4</sup>.

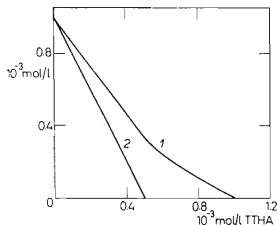
If the mixture of nickel(II) and cadmium(II) ions was titrated amperometrically, the shape of the resulting titration curves depended on time during which the reagent had reacted with the both metal ions. In the case when the reagent has been added stepwise, and the corresponding polarographic waves were recorded 3 minutes after the addition of each fraction of the reagent, the curves indicating the decrease of the concentration of free nickel(II) and cadmium(II) ions are shown in Fig. 2, curves 1 and 2. If, on the other hand, the titration was carried out slowly, (series of solutions corresponding to different points of the titration curve was prepared and these solutions were polarographed after a given time interval) resulting titration curves had the shape shown in Fig. 2, curves 4 and 5 (concentration of nonchelated cadmium and nickel ions was measured 250 min after the addition of each fraction of the reagent). Different course of the titration curves was explained by the proposal that immediately after the addition of the reagent a mixed binuclear chelate  $\text{CdNiX}^{2-}$  was formed. The mixed chelate then decomposed forming slowly the chelates  $\text{Ni}_2\text{X}^{2-}$  and  $\text{CdX}^{4-}$ , as expressed by the reactions



During the course of the described amperometric titration a new polarographic wave was observed, this wave had a half-wave potential more negative than that of nickel(II) in the same solution (Fig. 2, curves 3 and 6). The half-wave potential and the height of this wave changed with time. At the 1 : 1 : 1 molar ratio of Cd : Ni : X, the observed half-wave potential was  $-1.40 \text{ V}$  (s.c.e.) immediately after

Fig. 1  
Variation of Cadmium(II) and Nickel(II) Ions  
Concentration in Dependence of Amount of TTHA  
Reagent

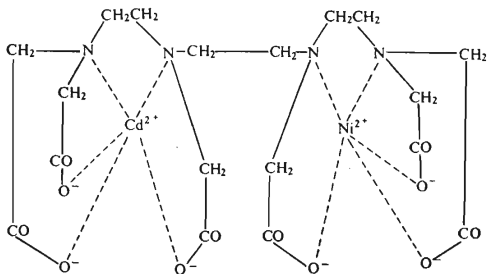
$C_{\text{Cd}} = C_{\text{Ni}} = 1.0 \cdot 10^{-3} \text{ mol/l}$ ;  $C_{\text{NH}_3} = 0.5 \text{ mol/l}$ .  
Variation of: 1 [ $\text{Cd}^{2+}$ ]; 2 [ $\text{Ni}^{2+}$ ].



mixing and reached a constant value  $-1.10$  V (S.C.E.) after 300 min. As shown on Fig. 2 (curves 3 and 6) the maximum height of the third wave was found in the solution of the composition Cd : Ni : X = 1 : 1 : 1. These findings led to the proposal that the third wave corresponded to the reduction of the mixed binuclear chelate. To verify this idea the formation and stability of the mixed binuclear chelate was further studied. More detailed examination of the nature of the third wave has not been done because this wave does not exist in the presence of an excess of the reagent and its half-wave potential and height was not constant as mentioned above.

### *Formation and Stability of the CdNiX<sup>2-</sup> Chelate*

The existence of the mixed binuclear chelate was first verified using the Schwarzenbach's technique<sup>3</sup> of the potentiometric neutralization of the mixture of reagent and metal ion. In the case of 1 : 1 metal to TTHA mixtures, the potentiometric neutralization curves indicated the formation of protonated 1 : 1 chelates of nickel and cadmium (Fig. 3, curves 2 and 4), similarly as has been observed by Bohigian and Martell<sup>5</sup>. In the case of cadmium-TTHA and nickel-TTHA 2 : 1 mixtures, the corresponding potentiometric curves (Fig. 3, curves 3 and 5) indicated the formation of binuclear chelates Cd<sub>2</sub>X<sup>2-</sup> and Ni<sub>2</sub>X<sup>2-</sup>; during the formation of these chelates all the available protons of the reagent were neutralized in one step. If the reaction mixture was composed of 1 : 1 : 1 mixture of cadmium, nickel and the reagent the resulting neutralization curve (Fig. 3, curve 6) had identical shape as the curves corresponding to the formation of nickel or cadmium binuclear chelates (Fig. 3, curves 3 and 5). This finding verified the proposal of the formation of the mixed binuclear chelate CdNiX<sup>2-</sup>. The given results led to the conclusion that optimum conditions for the formation of mixed binuclear chelate exist in the system



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which contained all three components (reagent,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  ions) in the molar ratio 1 : 1 : 1. In the system of such composition and with varied concentration of ammonia the polarographic waves of non-chelated cadmium and nickel ions were recorded six hours after mixing.

The first series of experiments was carried out as follows: one equivalent of nickel(II) salt was added to one equivalent of the reagent in the solution of given concentration of ammonia. After that one equivalent of cadmium salt was added into the resulting solution and the corresponding

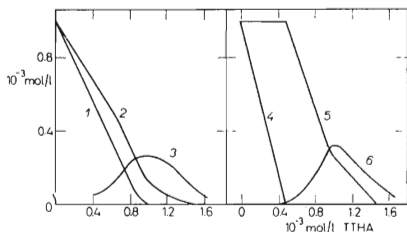


FIG. 2

Variation of Cadmium(II) and Nickel(II) Ions Concentration in Dependence of Amount of TTHA Reagent in Solution Containing Equimolar Amount of Cadmium and Nickel

$C_{\text{Cd}} = C_{\text{Ni}} = 1.0 \cdot 10^{-3}$  mol/l;  $C_{\text{NH}_3} = 0.5$  mol/l. Variation of ion (time after mixing): 1 [ $\text{Cd}^{2+}$ ] 3 min; 2 [ $\text{Ni}^{2+}$ ] 3 min; 3 [ $\text{Cd}^{2+}$ ] 250 min; 4 [ $\text{Ni}^{2+}$ ] 250 min.

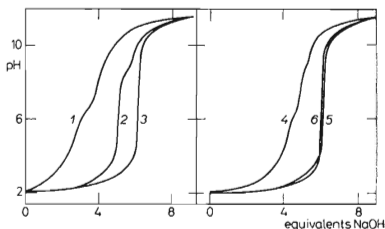


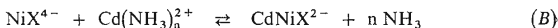
FIG. 3

Potentiometric Neutralization Titrations of Cadmium(II) and Nickel(II) Chelates of TTHA in 0.1M- $\text{KNO}_3$

1 Reagent alone; 2 Cd-TTHA 1 : 1, 3 Cd-TTHA 2 : 1, 4 Ni-TTHA 1 : 1; 5 Ni-TTHA 2 : 1, 6 Ni-Cd-TTHA 1 : 1 : 1; molar ratios of metal ion to ligand.

polarographic waves were recorded after suitable time interval. In the second case one equivalent of cadmium(II) salt was mixed with one equivalent of the reagent in ammoniacal solution and the same molar amount of nickel(II) salt was added to the resulting solution. As in the previous case the corresponding polarographic waves were recorded under identical conditions.

Under the assumption that the mixed binuclear chelate exists, the first series of experiments was described by the reaction



and the corresponding equilibrium constant  $K_B$  was defined by the equation

$$K_B = \frac{[\text{CdNiX}^{2-}][\text{NH}_3]^n}{[\text{NiX}^{4-}][\text{Cd}(\text{NH}_3)_n^{2+}]} \quad (1)$$

Because the stability constant of the  $\text{Cd}(\text{NH}_3)_n$  complex  $K_{\text{Cd}(\text{NH}_3)_n}$  is defined as

$$K_{\text{Cd}(\text{NH}_3)_n} = \frac{[\text{Cd}(\text{NH}_3)_n^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^n} \quad (2)$$

the equation (1) may be rewritten in the form

$$K_B = \frac{[\text{CdNiX}^{2-}][\text{NH}_3]^n}{[\text{NiX}^{4-}][\text{Cd}^{2+}]K_{\text{Cd}(\text{NH}_3)_n}[\text{NH}_3]^n} = \frac{K_{\text{CdNiX}}^{\text{Cd}}}{K_{\text{Cd}(\text{NH}_3)_n}} \quad (3)$$

The constant  $K_{\text{CdNiX}}^{\text{Cd}}$  in equation (3) was defined as

$$K_{\text{CdNiX}}^{\text{Cd}} = \frac{[\text{CdNiX}^{2-}]}{[(\text{Cd}^{2+})][\text{NiX}^{4-}]} \quad (4)$$

and this constant determines the stability of the mixed binuclear chelate  $\text{CdNiX}^{2-}$  formed according to the reaction



From equation (3) it is evident that the determination of the equilibrium constant  $K_B$  enables the calculation of the constant  $K_{\text{CdNiX}}^{\text{Cd}}$ .

For the calculation of the value of the equilibrium constant  $K_B$  using the experimentally obtained data, it was necessary to find the value corresponding to the equilibrium concentration of the species  $\text{CdNiX}^{2-}$ ,  $\text{NiX}^{4-}$  and  $\text{Cd}(\text{NH}_3)_n^{2+}$ . The concentration of these species was de-

terminated by the solution of mass balance equations, defining the total concentration of the reagent  $C_X$ , total concentration of nickel  $C_{Ni}$  and total concentration of cadmium  $C_{Cd}$ .

$$C_{Ni} = [Ni^{2+}] + \sum_{n=1}^6 [Ni(NH_3)_n^{2+}] + [CdNiX^{2-}] + [NiX^{4-}], \quad (5)$$

$$C_{Cd} = [Cd^{2+}] + [CdNiX^{2-}] + \sum_{n=1}^6 [Cd(NH_3)_n^{2+}] + [CdX^{4-}], \quad (6)$$

$$C_X = [X^{6-}] + [CdNiX^{2-}] + [NiX^{4-}] + [CdX^{4-}]. \quad (7)$$

The composition of the nickel and cadmium ammonia complexes depends on the concentration of ammonia and the number of bound  $NH_3$  groups was therefore expressed by the index  $n$ . Before the solution of the equations (5), (6), and (7), the following approximation was made: the concentration of free nickel(II) and cadmium(II) ions was neglected (presence of an excess of ammonia and presence of the reagent). The same approximation was made for the concentration of free reagent due to relatively high value of the stability constants of chelates involved. Under these conditions equations (5), (6), and (7) were simplified to

$$C_{Ni} = b + [CdNiX^{2-}] + [NiX^{4-}], \quad (5a)$$

$$C_{Cd} = a + [CdNiX^{2-}] + [CdX^{4-}], \quad (6a)$$

$$C_X = [NiX^{4-}] + [CdX^{4-}] + [CdNiX^{2-}], \quad (7a)$$

where  $b$  means the polarographically measured concentration of nickel ammonia complex and  $a$  the measured concentration of the cadmium ammonia complex. Because the measurement was carried out in the system containing nickel, cadmium and reagent in the molar ratio 1 : 1 : 1, the equation also hold

$$C_{Ni} = C_{Cd} = X_X. \quad (8)$$

The solution of equations (5a), (6a), (7a), and (8) gives

$$[NiX^{4-}] = a, \quad (9)$$

$$[CdNiX^{2-}] = C_{Ni} - a - b. \quad (10)$$

After the substitution of the expressions (9) and (10) into equation (3) the constant  $K_B$  may be expressed as

$$K_B = (C_{Ni} - a - b) [NH_3]^n / a^2. \quad (11)$$

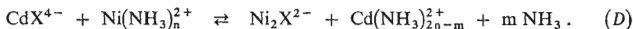
In the calculation of the value of the constant  $K_B$  according to equation (11) instead of the equilibrium concentration of ammonia  $[NH_3]$  the total concentration of ammonia was taken because this approximation results in a minimal error (concentration of the metal ions  $10^{-3}M$ , concentration of ammonia  $10^{-1} - 4M$ ). The value of  $n$  in equation (11), which also means the number of  $NH_3$  groups bound to the

cadmium(II) ion (reaction (B)) was determined from the known concentration of ammonia using the distribution diagram for cadmium ammonia complexes<sup>6</sup>. Values of  $K_B$  calculated according to the equation (11) corresponding to various concentrations of ammonia are presented in graphical form in Fig. 4, curve 1. This dependence shows that the value of  $K_B$  is constant in the interval of ammonia concentrations from 0.2 to 0.8 mol/l and has the value  $2.0 \cdot 10^3$ . The constant value of the calculated  $K_B$  constant verifies the validity of the reaction (B) in the given concentration interval for ammonia.

The stability constant of the mixed binuclear chelate  $K_{CdNiX}^{Cd}$  was determined from the known value of the constant  $K_B$  using equation (3). By the substitution of the value of  $K_B$  into equation (3) the log value of the constant  $K_{CdNiX}^{Cd}$  was calculated as 9.2. In this calculation, number three was used as the value of  $n$ , because at the ammonia concentration from 0.2 to 0.8 mol/l the prevailing form of the cadmium ammonia complex is  $Cd(NH_3)_3$  (ref.<sup>6</sup>). Relatively high value of the stability constant  $K_{CdNiX}^{Cd}$  verified that under optimum conditions (concentration of ammonia and 1 : 1 : 1 molar ratio of all involved components of the binuclear chelate) a stable mixed chelate was formed as expressed by the reaction (C). The formation of the mixed chelate  $CdNiX^{2-}$  resulting from the reaction of  $CdX^{4-}$  chelate with nickel ammonia complex was studied in the second series of experiments. In this case it was observed that not only the binuclear mixed chelate was formed but also small amounts of  $Cd^{2+}$  ions were released from the  $CdX^{4-}$  chelate.

#### *Reaction of $CdX^{4-}$ Chelate with Excess of Nickel(II) Ions*

In the experiments during which the solution of nickel salt was stepwise added to the Cd-TTHA chelate in ammoniacal medium, dependence of the amount of free (nonchelated) cadmium(II) and nickel(II) ions on the concentration of the added nickel solution was observed. Such dependence is shown in Fig. 5, curves 1, 2 and 3, 4. The interpretation of these dependences gave the result that two equivalents of nickel released one equivalent of free cadmium(II) ions from the  $CdX^{4-}$  chelate. This process has been formulated by the substitution reaction



The equilibrium constant  $K_D$  corresponding to the reaction (D) was defined as

$$K_D = \frac{[Ni_2X^{2-}][Cd(NH_3)_{2n-m}^{2+}][NH_3]^m}{[CdX^{4-}][Ni(NH_3)_n^{2+}]} = \frac{K_{Ni_2X} K_{Cd(NH_3)_{2n-m}}}{K_{CdX} K_{Ni(NH_3)_n}^2} \quad (12)$$

where the terms  $K_{Ni_2X}$ ,  $K_{Cd(NH_3)_{2n-m}}$ ,  $K_{CdX}$  and  $K_{Ni(NH_3)_n}$  correspond to the stability constant of the 1 : 2 nickel-TTHA chelate, cadmium ammonia complex with  $(2n - m)$



$\text{NH}_3$  groups, 1:1 cadmium-TTHA chelate and nickel-ammonia complex with  $n$   $\text{NH}_3$  groups, respectively. These stability constants are defined by equations similar to equation (4). The values of  $n$  and  $m$  were determined from the distribution curves for nickel and cadmium ammonia complexes for a given concentration of ammonia<sup>6</sup>.

The establishment of the equilibrium expressed by the reaction (D) takes some time, the rate of this reaction was found to depend on the concentration of ammonia. The experimental data (concentration of nonchelated cadmium and nickel ions) were therefore measured three hours

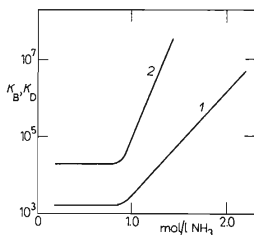


FIG. 4

Values of the Equilibrium Constants  $K_B$  and  $K_D$  in Dependence on Ammonia Concentration  
1  $K_B$ ; 2  $K_D$ .

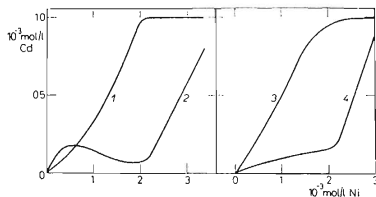


FIG. 5

Dependence of the Amount of Nonchelated Cadmium(II) and Nickel(II) Ions on the Total Concentration of Nickel for the Reaction of  $\text{CdX}^{4-}$  Chelate with Nickel(II)

Change of the concentration of nonchelated ion of: 1 Cd,  $C_{\text{NH}_3} = 0.2$  mol/l; 2 Ni,  $C_{\text{NH}_3} = 0.2$  mol/l; 3 identical with curve 1,  $C_{\text{NH}_3} = 1.0$  mol/l; 4 identical with curve 2,  $C_{\text{NH}_3} = 1.0$  mol/l. Measured 12 hours after mixing.

after mixing the reacting components. The system was determined by the mass balance equations

$$C_{Cd} = [Cd^{2+}] + [CdX^{4-}] + [CdNiX^{2-}] + \sum_{\substack{n=1 \\ m=1}}^6 [Cd(NH_3)_{2n-m}^{2+}], \quad (13)$$

$$C_{Ni} = [Ni^{2+}] + [NiX^{4-}] + 2[Ni_2X^{2-}] + [CdNiX^{2-}] + \sum_{n=1}^6 [Ni(NH_3)_n^{2+}], \quad (14)$$

$$C_X = [X^{6-}] + [NiX^{4-}] + [CdX^{4-}] + [Ni_2X^{2-}] + [CdNiX^{2-}], \quad (15)$$

$$C_{NH_3} = [NH_3] + n[Ni(NH_3)_n^{2+}] + (2n - m)[Cd(NH_3)_{2n-m}^{2+}]. \quad (16)$$

Under the experimental conditions the concentration of free cadmium(II) and nickel(II) ions may be neglected due to the presence of large excess of ammonia and due to the presence of the reagent. Similarly the concentration of free reagent  $X^{6-}$  may be neglected due to the high value of the stability constants of nickel and cadmium chelates. If polarographically measured concentration of the cadmium ammonia complex is expressed as  $a$  and the measured concentration of the nickel ammonia complex as  $b$ , the equations (13)–(15) may be written in simplified form

$$C_{Cd} = [CdX^{4-}] + [CdNiX^{2-}] + a, \quad (13a)$$

$$C_{Ni} = [NiX^{4-}] + 2[Ni_2X^{2-}] + [CdNiX^{2-}] + b, \quad (14a)$$

$$C_X = [NiX^{4-}] + [CdX^{4-}] + [Ni_2X^{2-}] + [CdNiX^{2-}]. \quad (15a)$$

Because during all measurements the total concentration of cadmium was equal to the total concentration of the reagent, the equation

$$C_{Cd} = C_X \quad (17)$$

also holds.

It can be supposed that practically all chelated nickel is bound as  $Ni_2X^{2-}$  ( $C_{Ni} > C_X$ ). Under these conditions the concentration of  $NiX^{4-}$  may be neglected and the solution of equations (13a), (14a), (15a) and (17) for the concentration of the species involved gave these results

$$[Ni_2X^{2-}] = a, \quad (18)$$

$$[CdNiX^{2-}] = C_{Ni} - 2a - b, \quad (19)$$

and

$$[CdX^{4-}] = C_{Cd} - C_{Ni} + a + b. \quad (20)$$

By the substitution of expressions (18)–(20) into equation (12) the equilibrium constant  $K_D$  was expressed as

$$K_D = \frac{a^2[NH_3]^m}{(C_{Cd} - C_{Ni} + a + b)b^2}. \quad (21)$$

Equation (21) was used for the calculation of the value of the equilibrium constant

$K_D$  and corresponding values for various concentrations of ammonia are presented in Fig. 4, curve 2.

In these calculations the total concentration of ammonia was used instead of the equilibrium concentration of ammonia  $[\text{NH}_3]$  (see equation (17), large excess of ammonia compared with the concentration of metal ions). As seen from Fig. 4, curve 2,  $K_D$  is constant in the concentration range of ammonia from 0.3 to 0.8 mol/l and has the value  $2.7 \cdot 10^4$ . According to the equation (12) the value of stability constant of the 1 : 1 cadmium-TTHA chelate may be calculated using the previously determined value of the constant  $K_D$ , the known value of the stability constant of the 2 : 1 nickel-TTHA chelate and the tabulated values of cadmium and nickel ammonia complexes. The log value of the stability constant of 2 : 1 nickel-TTHA chelate was reported by Bohigian and Martell<sup>5</sup> to be 29.5. Under these conditions the value of  $\log K_{\text{Cd}}$  was calculated as 18.5, according to equation (12). The obtained result is in agreement with that reported recently by Souček, Cheng and Droll<sup>7</sup>. The value of the constant  $K_{\text{CdX}}$  calculated on the basis of the substitution reaction (D) is not as accurate as this constant calculated on the basis of potentiometrically obtained data<sup>5,7</sup>. The equilibrium study however verified the proposal of the formation of the mixed binuclear chelate  $\text{CdNiX}^{2-}$  and the release of free (nonchelated) cadmium(II) ions during the reaction studied.

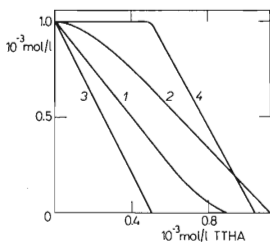


FIG. 6

Variation of Zinc(II) and Nickel(II) Ions Concentration in Dependence of Amount of TTHA Reagent in Solution Containing Equimolar Amount of Zinc and Nickel

$C_{\text{Zn}} = C_{\text{Ni}} = 1.0 \cdot 10^{-3}$  mol/l;  $C_{\text{NH}_3} = 1.0$  mol/l. Variation of ion (time after mixing) 1  $[\text{Ni}^{2+}]$ , 3 min; 2  $[\text{Zn}^{2+}]$ , 3 min; 3  $[\text{Ni}^{2+}]$ , 12 h; 4  $[\text{Zn}^{2+}]$ , 12 h.

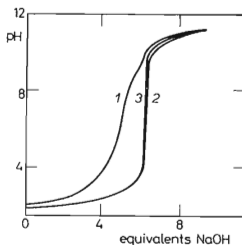


FIG. 7

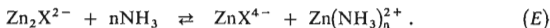
Potentiometric Neutralization Titrations of Zn(II) Chelates of TTHA in 0.1M-KNO<sub>3</sub>

1 Zn-TTHA 1 : 1; 2 Zn-TTHA 2 : 1, 3 Zn-Ni TTHA 1 : 1 : 1 molar ratios of metal ion to ligand.

## SYSTEM CONTAINING ZINC(II) AND NICKEL(II) IONS AND TTHA REAGENT

*Preliminary Experiments*

Amperometric titrations of zinc(II) ions with TTHA reagent in ammoniacal medium, carried out under identical conditions as in the case of cadmium or nickel, have shown the formation of the  $Zn_2X^{2-}$  chelate. Amperometric titration curve of zinc was found to be identical with that of nickel. Contrary to the behaviour of the  $Ni_2X^{2-}$  chelate it was observed that a small fraction of the  $Zn^{2+}$  ions was released from the  $Zn_2X^{2-}$  chelate in the presence of ammonia. This phenomenon was explained by the proposed reaction



Calculation of the value of the equilibrium constant of the reaction (E) gave the value approx.  $10^{-5}$  for the concentration of ammonia from 0.5 to 1.75M. This value means that the amount of zinc(II) ions released from the  $Zn_2X^{2-}$  chelate is under given experimental conditions very small compared with the amount of zinc(II) ions released by the substitution.

As in the previous case, the amperometric titrations of the mixture of zinc(II) and nickel(II) showed the time dependence of the studied reaction. Titration curves presented in Fig. 6 show the course of the titration of the mixture zinc(II) and nickel(II) ions. Curves 1 and 2 correspond to the titration carried out normally, curves 3 and 4 to "slow" titration (solutions, the composition of which correspond to a given point of the titration curve, were prepared and polarographed after 12 hours). Similarly as for the system containing nickel(II), cadmium(II) and TTHA reagent, the formation of mixed binuclear chelate  $ZnNiX^{2-}$  was proposed to explain the difference in the shapes of the corresponding titration curves.

*Formation and Stability of the  $ZnNiX^{2-}$  Chelate*

The formation of the mixed binuclear chelate was first studied using the Schwarzenbach's method described in the first part of this work. Curve 3 in Fig. 7 corresponding to the neutralisation of 1 : 1 : 1 molar ratio mixture  $Zn^{2+}$ ,  $Ni^{2+}$  and TTHA, verified the proposal of the formation of  $ZnNiX^{2-}$  chelate, because curve 3 has identical shape with curve 2, corresponding to the neutralization of the reagent and zinc mixture in the molar ratio 1 : 2.

Further studies were carried out with the equimolar mixture of nickel(II) ions and the reagent in the solution of ammonia of a given concentration (or with equimolar mixture of zinc(II) ions and the reagent). To these mixtures was added one equivalent of zinc(II) ions (or nickel(II) ions) and the concentrations of nonchelated

metal ions were determined polarographically. In the first case the formation of the mixed binuclear chelate was expressed by the reaction



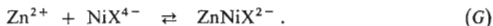
The equilibrium constant of the reaction (F) was defined as

$$K_F = [\text{ZnNiX}^{2-}] [\text{NH}_3]^n / [\text{NiX}^{4-}] [\text{Zn}(\text{NH}_3)_n^{2+}] = K_{\text{ZnNiX}}^{\text{Zn}} / K_{\text{Zn}(\text{NH}_3)_n}. \quad (22)$$

In the equation (22)  $K_{\text{Zn}(\text{NH}_3)_n}$  is the stability constant of the complex  $\text{Zn}(\text{NH}_3)_n$  and  $K_{\text{ZnNiX}}^{\text{Zn}}$  the stability constant of the mixed chelate  $\text{ZnNiX}^{2-}$ , defined by the equation

$$K_{\text{ZnNiX}}^{\text{Zn}} = [\text{ZnNiX}^{2-}] / [\text{Zn}^{2+}] [\text{NiX}^{4-}]. \quad (23)$$

Equation (23) is based on the validity of reaction (G) describing the formation of the mixed chelate



The stability constant of the mixed chelate  $K_{\text{ZnNiX}}^{\text{Zn}}$  may be determined under the presumption that the equilibrium constant  $K_F$  was previously determined and that the stability of the  $\text{Zn}(\text{NH}_3)_n$  complex is known. The mass balance equations, defining the total concentration of the species involved, are

$$C_X = [\text{ZnNiX}^{2-}] + [\text{NiX}^{4-}] + [\text{ZnX}^{4-}] + [\text{X}^{6-}], \quad (24)$$

$$C_{\text{Ni}} = [\text{ZnNiX}^{2-}] + [\text{NiX}^{4-}] + \sum_{m=1}^6 [\text{Ni}(\text{NH}_3)_m^{2+}] + [\text{Ni}^{2+}], \quad (25)$$

$$C_{\text{Zn}} = [\text{ZnNiX}^{2-}] + [\text{ZnX}^{4-}] + \sum_{n=1}^4 [\text{Zn}(\text{NH}_3)_n^{2+}] + [\text{Zn}^{2+}]. \quad (26)$$

Due to the presence of ammonia the equilibrium concentration of free nickel(II) and zinc(II) ions was neglected in equations (25) and (24) and also the concentration of nonreacted ligand  $\text{X}^{6-}$  was neglected in equation (26) due to the high stability of nickel and zinc chelates.

In respect to these approximations equations (24), (25) and (26) were simplified as follows

$$C_X = [\text{ZnNiX}^{2-}] + [\text{NiX}^{4-}] + [\text{ZnX}^{4-}], \quad (27)$$

$$C_{\text{Ni}} = [\text{ZnNiX}^{2-}] + [\text{NiX}^{4-}] + b, \quad (28)$$

$$C_{\text{Zn}} = [\text{ZnNiX}^{2-}] + [\text{ZnX}^{4-}] + d, \quad (29)$$

where  $d$  means the polarographically determined concentration of the zinc-ammonia complex and  $b$  has the same meaning as in the first part of this work. Because under the experimental conditions the equation

$$C_{\text{Zn}} = C_{\text{Ni}} = C_X, \quad (30)$$

also holds, we have

$$[\text{NiX}^{4-}] = d \quad (31)$$

and

$$[\text{ZnNiX}^{2-}] = C_{\text{Ni}} - d - b. \quad (32)$$

These results are identical with that obtained in the study of the nickel-cadmium-TTHA system with the exception that  $b = 0$  in the system zinc-nickel-TTHA.

After the substitution of expressions (31) and (32) into equation (22) the equation

$$K_F = (C_{\text{Ni}} - d - b) [\text{NH}_3]^{-n} \frac{1}{d^2} \quad (33)$$

was obtained, where the number 4 was used for  $n$ , because in the studied concentration range of ammonia the complex  $\text{Zn}(\text{NH}_3)_4^{2+}$  prevailed. Due to relatively high concentration of ammonia, its total concentration (instead of equilibrium concentration  $[\text{NH}_3]$ ) was applied in the calculation of the equilibrium constant  $K_F$  according to the equation (33).

The calculated value of the constant  $K_F$  for various concentrations of ammonia is given in Table I. Using this value (average value  $K_F$  is  $6.7 \cdot 10^4$ ) the stability constant of the mixed chelate  $\text{ZnNiX}^{2-}$  was determined according to equation (23)

$$\log K_{\text{ZnNiX}}^{\text{Zn}} = \log K_F + \log K_{\text{Zn}(\text{NH}_3)_n} = 13.80. \quad (34)$$

In the second series of experiments (addition of nickel(II) salt into the ammoniacal solution of  $\text{ZnX}^{4-}$  chelate) the formation of a stable mixed binuclear chelate was

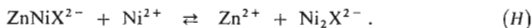
TABLE I

Values of the Constant  $K_F$  Calculated according to Eq. (33)

$$C_{\text{Ni}} = 1.01 \cdot 10^{-3} \text{ mol/l}, C_{\text{X}} = 1.01 \cdot 10^{-3} \text{ mol/l}, n = 4.$$

$C_{\text{NH}_3}$ mol/l	$C_{\text{Zn}}$ mol/l · 10 <sup>3</sup>	log $K_F$
0.25	1.01	3.65
0.50	0.96	4.64
0.50	1.01	4.69
0.50	1.03	4.85
0.50	1.05	5.10
0.75	0.96	5.10
0.75	1.01	5.11
1.00	1.01	5.52

also observed. Fig. 8 illustrates the variation of the concentration of nonchelated zinc(II) and nickel(II) ions during the stepwise addition of nickel(II) salt into the ammoniacal solution of  $ZnX^{4-}$  chelate. At the beginning of the addition of nickel solution no nickel or zinc waves were observed, which verified the formation of the  $ZnNiX^{2-}$  chelate. If, on the other hand, more than one equivalent of nickel was added, the course of the curves in Fig. 8 showed the release of zinc(II) ions from the mixed chelate according to the reaction



#### Reaction of $Zn_2X^{2-}$ Chelate with Nickel(II) Ions

The stepwise addition of nickel(II) ions into the ammoniacal solution of  $Zn_2X^{2-}$  chelate resulted in the release of free (nonchelated) zinc(II) ions. One equivalent of nickel released one equivalent of zinc ions as shows in Fig. 9 (experimental data were obtained by polarographic measurement 12 hours after mixing of all components). The corresponding substitution equilibrium was formulated by the reaction

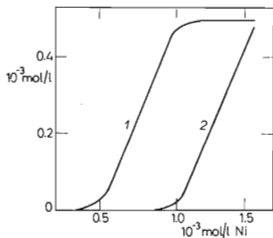
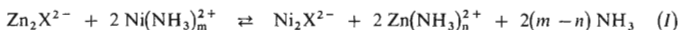


FIG. 8

Dependence of the Amount of Nonchelated Zn(II) and Ni(II) Ions on the Total Concentration of Ni for the Reaction of  $ZnX^{4-}$  Chelate with Ni

Change of the concentration of nonchelated ion of: 1 Zn(II),  $C_{NH_3} = 0.5$  mol/l; 2 Ni(II),  $C_{NH_3} = 0.5$  mol/l. Measured 12 hours after mixing.

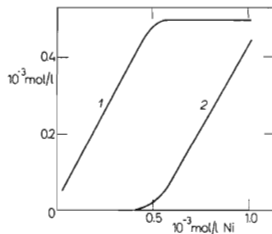


FIG. 9

Dependence of the Amount of Nonchelated Zn(II) and Ni(II) Ions on the Total Concentration of Ni for the Reaction of  $Zn_2X^{2-}$  Chelate with Ni

Ion of: 1 Zn(II),  $C_{NH_3} = 0.5$  mol/l; 2 Ni(II),  $C_{NH_3} = 0.5$  mol/l. Measured 12 hours after mixing.

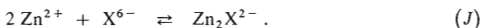
and the corresponding equilibrium constant

$$K_1 = \frac{[\text{Ni}_2\text{X}^{2-}][\text{Zn}(\text{NH}_3)_n^{2+}]^2[\text{NH}_3]^{2(m-n)}}{[\text{Zn}_2\text{X}^{2-}][\text{Ni}(\text{NH}_3)_m^{2+}]^2} = \frac{K_{\text{Ni}_2\text{X}} \cdot K_{\text{Zn}(\text{NH}_3)_n}^2}{K_{\text{Zn}_2\text{X}} \cdot K_{\text{Ni}(\text{NH}_3)_m}^2}, \quad (34)$$

where the stability constants of zinc and nickel ammonia complexes,  $K_{\text{Zn}(\text{NH}_3)_n}$  and  $K_{\text{Ni}(\text{NH}_3)_m}$  are defined by the equations similar to equation (2). Values of these constants are tabulated and also the value of the stability constant of the  $\text{Ni}_2\text{X}^{2-}$  chelate is known<sup>5</sup>. After the determination of the equilibrium constant  $K_1$ , it was therefore possible to calculate the value of the stability constant of the  $\text{Zn}_2\text{X}^{2-}$  chelate. This constant was defined by the equation

$$K_{\text{Zn}_2\text{X}} = \frac{[\text{Zn}_2\text{X}^{2-}]}{[\text{Zn}^{2+}]^2[\text{X}^{6-}]} \quad (35)$$

corresponding to the reaction



The equilibrium constant  $K_1$  cannot be determined without several approximations. As in the case of the Cd-Ni-X system the mass balance equations were formulated as

$$C_{\text{Ni}} = [\text{Ni}^{2+}] + \sum_{m=1}^6 [\text{Ni}(\text{NH}_3)_m^{2+}] + [\text{NiX}^{4-}] + 2[\text{Ni}_2\text{X}^{2-}] + [\text{ZnNiX}^{2-}] \quad (36)$$

$$C_{\text{Zn}} = [\text{Zn}^{2+}] + \sum_{m=1}^4 [\text{Zn}(\text{NH}_3)_m^{2+}] + [\text{ZnX}^{4-}] + 2[\text{Zn}_2\text{X}^{2-}] + [\text{ZnNiX}^{2-}] \quad (37)$$

$$C_{\text{X}} = [\text{Ni}^{4-}] + [\text{Ni}_2\text{X}^{2-}] + [\text{ZnX}^{4-}] + [\text{Zn}_2\text{X}^{2-}] + [\text{ZnNiX}^{2-}] + [\text{X}^{6-}]. \quad (38)$$

Under the given experimental conditions also the equation

$$C_{\text{Zn}} = 2C_{\text{X}} \quad (39)$$

holds. Similarly as in the solution of the equations describing the system Cd-Ni-X, the equilibrium concentration of free (nonchelated) nickel and zinc ions was neglected as was the concentration of free ligand  $[\text{X}^{6-}]$ . Even after such approximations the system of equations (36)–(38) cannot be solved and therefore the equilibrium concentrations of  $\text{ZnNiX}^{2-}$  and  $\text{Zn}^{4-}$  chelates were neglected. This approximation was possibly due to the fact that under the experimental conditions ( $2C_{\text{Zn}} = C_{\text{Ni}}$ ) all amount of  $\text{ZnNiX}^{2-}$  chelate was transformed to  $\text{Ni}_2\text{X}^{2-}$  chelate in the equilibrium state. The experiments also showed that practically all amount of zinc was present in the form of ammonia complex in the equilibrium state. The equations (36), (37) and (38) were therefore simplified:

$$C_{\text{Ni}} = 2[\text{Ni}_2\text{X}^{2-}] + b + [\text{NiX}^{4-}], \quad (36)$$



$$C_{Zn} = 2[Zn_2X^{2-}] + d, \quad (37)$$

$$C_X = [Ni_2X^{2-}] + [Zn_2X^{2-}]. \quad (38)$$

After the solution of these equations for  $Ni_2X^{2-}$  and  $Zn_2X^{2-}$  and by the substitution of the results into equation (34), the equilibrium constant  $K_I$  was expressed as

$$K_I = \frac{(C_{Ni} - b) d^2 [NH_3]^{2(m-n)}}{(C_{Zn} - d) b^2}. \quad (40)$$

The value of the equilibrium constant  $K_I$  calculated at various concentrations of ammonia is shown in Table II. With the use of equation (34) the stability constant of the  $Zn_2X^{2-}$  chelate was calculated giving for  $K_{Zn_2X}$  the value 27.3; this result agrees very well with that reported by other authors<sup>7,8</sup>.

#### SYSTEM CONTAINING CADMIUM(II) AND ZINC(II) IONS AND THE REAGENT

Preliminary experiments carried out in the system containing zinc(II) and cadmium(II) ions, reagent and ammonia showed evidence for the formation of the mixed binuclear chelate  $CdZnX^{2-}$ . More detailed polarographic measurements, carried out identically as in previous cases verified this finding. Some results obtained in these measurements are summarized in Table III.

TABLE II

Values of the Equilibrium Constant  $K_I$  for Various Concentration of Ammonia Calculated according to Eq. (40)

$$C_{Zn} = 4.0 \cdot 10^{-4} \text{ mol/l}; C_X = 2 \cdot 10^{-4} \text{ mol/l}; n = 4; m = 5.$$

$C_{Ni}$ mol/l · 10 <sup>4</sup>	$C_{NH_3}$ mol/l	log $K_I$
3.00	0.1	2.04
3.50	0.5	3.31
3.75	0.5	3.19
4.00	0.5	3.03
4.50	0.5	3.10
3.50	1.0	3.62
4.00	1.0	3.48
4.25	1.0	3.39
4.50	1.0	3.38
3.50	2.0	5.31

TABLE III

Experimental Data Obtained in the Study of the Reaction of  $\text{CdX}^{4-}$  Chelate with Zinc(II) Ions  
 $C_{\text{Cd}} = C_{\text{X}} = 5.0 \cdot 10^{-4}$  mol/l.

$C_{\text{NH}_3}$ mol/l	$C_{\text{Zn}}$ (mol/l) · 10 <sup>4</sup>	$\text{Cd}^{2+}$ (mol/l) · 10 <sup>4</sup>	$\text{Zn}^{2+}$ (mol/l) · 10 <sup>4</sup>	log $K_{\text{K}}$
0.25	5.42	0.73	0.57	3.88
0.25	8.13	1.12	2.28	—
0.50	2.71	0.47	0.34	3.12
0.50	5.42	1.00	0.90	3.66
0.50	10.80	1.67	4.77	—
0.75	2.71	0.53	0.43	3.68
0.75	5.42	1.10	0.96	3.32
0.75	10.80	1.80	4.70	—
1.00	2.71	0.65	0.45	4.21
1.00	5.42	1.22	1.08	4.63

#### Formation and Stability of the Mixed Chelate $\text{CdZnX}^{2-}$

The formation of the mixed binuclear chelate  $\text{CdZnX}^{2-}$  in ammoniacal medium was expressed by the reaction



and the corresponding equilibrium constant was defined as

$$K_{\text{K}} = \frac{[\text{CdZnX}^{2-}][\text{NH}_3]^n}{[\text{CdX}^{4-}][\text{Zn}(\text{NH}_3)_n^{2+}]} = \frac{K_{\text{CdZnX}}^{\text{Zn}}}{K_{\text{Zn}(\text{NH}_3)_n}} \quad (41)$$

$K_{\text{CdZnX}}^{\text{Zn}}$  is the stability constant of the mixed chelate by the expression

$$K_{\text{CdZnX}}^{\text{Zn}} = \frac{[\text{CdZnX}^{2-}]}{[\text{CdX}^{4-}][\text{Zn}^{2+}]} \quad (42)$$

Similarly as in previous cases the mass balance equations describing the system studied were formulated by the equations

$$C_{\text{Zn}} = d + [\text{CdZnX}^{2-}] + [\text{ZnX}^{4-}], \quad (43)$$

$$C_{\text{Cd}} = a + [\text{CdZnX}^{2-}] + [\text{CdX}^{4-}], \quad (44)$$

$$C_X = [\text{CdX}^{4-}] + [\text{ZnX}^{4-}] + [\text{CdZnX}^{2-}], \quad (45)$$

$$C_{\text{Cd}} = C_X. \quad (46)$$

Because the experimental conditions are identical as in previous cases concentrations of free metal ions and free reagent were neglected. It can be further supposed that only minimal amount of the  $\text{Zn}_2\text{X}^{2-}$  chelate is formed under the described conditions and therefore the equilibrium concentration of  $\text{Zn}_2\text{X}$  chelate was also neglected. Solution of equilibrium concentration of  $\text{Zn}_2\text{X}$  chelate was also neglected. Solution of the equations (43)–(46) for  $\text{CdX}^{4-}$  and  $\text{CdZnX}^{2-}$  gives:

$$[\text{CdX}^{4-}] = C_{\text{Cd}} - C_{\text{Zn}} + d \quad (47)$$

$$[\text{CdZnX}^{2-}] = C_{\text{Zn}} - a - d. \quad (48)$$

By the substitution of expressions (47) and (48) into equation (41) the constant  $K_K$  was expressed as

$$K_K = \frac{(C_{\text{Zn}} - a - d) [\text{NH}_3]^n}{(C_{\text{Cd}} - C_{\text{Zn}} + d) d}. \quad (49)$$

Values of  $K_K$  for various concentration of ammonia calculated according to the equation (49) are presented in Table III. The average value of  $\log K_K$  is 3.5 for the concentration range of ammonia from 0.25 to 0.75 mol/l. So determined value of the equilibrium constant  $K_K$  enabled to calculate the value of the stability constant of the mixed chelate  $\text{CdZnX}^{2-}$ . Using the equation (41) the value of  $\log K_{\text{CdZnX}}^{\text{Zn}}$  was calculated to be 12.6.

#### Reaction of $\text{CdX}^{4-}$ Chelate with Excess of Zinc(II) Ions

Due to the difference of the stability constants of  $\text{Zn}_2\text{X}^{2-}$  chelate ( $\log K_{\text{Zn}_2\text{X}} = 27.3$ ) and  $\text{CdX}^{4-}$  chelate ( $\log K_{\text{CdX}} = 18.5$ ), one would expect the release of cadmium(II) ions from the  $\text{CdX}^{4-}$  chelate and the formation of  $\text{Zn}_2\text{X}^{2-}$  chelate as the result of the reaction of  $\text{CdX}^{4-}$  chelate with zinc(II) ions in ammoniacal medium. The experiments carried out at various concentrations of ammonia and with various molar ratios of  $\text{CdX}^{4-}$  to  $\text{Zn}^{2+}$  showed however that only small fraction of cadmium(II) ions was released from the  $\text{CdX}^{4-}$  chelate. For the proposed the reaction



the equilibrium constant is expressed by the equation

$$K_L = \frac{[\text{Cd}(\text{NH}_3)_4^{2+}] [\text{Zn}_2\text{X}^{2-}] [\text{NH}_3]^4}{[\text{CdX}^{4-}] [\text{Zn}(\text{NH}_3)_4^{2+}]^2} = \frac{K_{\text{Cd}(\text{NH}_3)_4} \cdot K_{\text{Zn}_2\text{X}}}{K_{\text{Zn}(\text{NH}_3)_4}^2 \cdot K_{\text{CdX}}}. \quad (50)$$

The value of the constant  $K_L$  calculated from the known values of the stability constants of zinc and cadmium ammonia complexes and zinc and cadmium TTHA chelates was very small ( $\log K_L \approx -2$ ). These results verified the experimental findings; equilibrium expressed by the reaction ( $L$ ) is shifted to the left hand side. This phenomenon is due to the presence of ammonia in the system examined. Experimentally it has been found that when ammonia was replaced by acetate buffer solution, free cadmium(II) ions were released from Cd-TTHA chelate quantitatively.

Besides the reaction systems described above, the substitution equilibria involving  $CdX^{4-}$  chelate and cobalt(II) or copper(II) or lanthanum ions were examined. In all cases the existence of mixed binuclear chelates was observed. Mixed chelates of TTHA reagent are stable species compared with similar type of EDTA chelates, which exist only as reaction intermediates<sup>9</sup>.

A reasonable arrangement of the mixed chelate  $CdNiX^{2-}$  is illustrated by (I); in this arrangement both metal ions share equally the basic nitrogen atoms and the negative charges. The evaluation of the mechanism of the substitution reactions described is presented in a separate paper.

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