

## INFLUENCE OF COPPER IONS ON THE RATE OF METAL EXCHANGE REACTION OF CADMIUM(II) TRIETHYLENETETRAMINEHEXAACETATE CHELATES

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The rate of the substitution reaction between mono or binuclear cadmium(II) triethylenetetraminehexaacetate and nickel(II) ions is modified (acceleration or inhibition) in the presence of trace amounts of copper(II) ions. An attempt was made to explain this effect by the formation of mixed binuclear chelate Cu-Cd-ligand and by its' reactions with nickel(II) ions present in excess in the reaction system.

The kinetic approach to analysis has been successfully applied to the detection and determination of traces of metals which show catalytic properties. The main reaction in which the concentration of participated species is monitored in the dependence of time is termed indicator reaction. Many of the indicator reactions are published in the literature<sup>1-3</sup>; the most widely applicable indicator reactions are oxidation-reduction reactions involving oxidation by  $\text{H}_2\text{O}_2$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{MnO}_4^-$  etc. Great interest has been recently paid to the analytical utilization of the complexation reactions accompanied with catalytic phenomena<sup>4,5</sup> and to the analytical utilization of the modifying effects of ligands on the catalytic action of metal ions<sup>1,6</sup>. In the paper are described effects of some metal ions on the rate of the substitution reactions involving the chelate-forming reagent which forms mono- and binuclear chelates.

### EXPERIMENTAL

#### Reagents and Apparatus

The solution of triethylenetetraminehexaacetic acid (TTHA,  $\text{H}_6\text{X}$ ) was prepared from the A.g. chemical (Dojin Pharmaceutical Laboratories, Japan) and standardized by amperometric titration with zinc solution. Solution of mono- and binuclear Cd-TTHA chelates was prepared by mixing of appropriate amounts of the solution of  $\text{Cd}^{2+}$  ions and the reagent. Solutions of  $10^{-5}\text{M}$  copper(II) nitrate were prepared before each measurement by the dilution of the  $10^{-3}\text{M}$  solution of  $\text{Cu}(\text{NO}_3)_2$ . All other solutions were prepared from a.g. chemicals. Twice distilled water was used for all measurements. Sodium perchlorate was used to adjust the ionic strength 0.1.

Polarographs OH-104 (Radelkis, Hungary) and Polarecord E 261 (Metrohm, Herisau) were used for recording square-wave and d.c. polarographic curves, respectively. The temperature of

the solutions was maintained at 22°C by means of a thermostat (Ministat-607, MTA, Hungary). The pH values were measured with a glass electrode using the pH meter PHM-25 (Radiometer, Denmark).

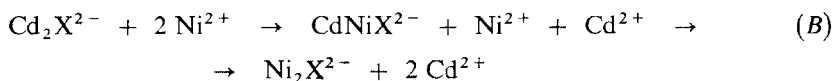
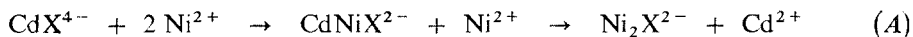
### Procedure

Reaction between Cd-TTHA chelates and nickel(II) ions were followed by the polarographic (d.c. or square-wave technique) measurement of the concentration of released  $\text{Cd}^{2+}$  ions in the time dependence. The reaction mixture containing buffer solution, sodium perchlorate and the chelate was placed in the thermostated cell and dissolved oxygen was removed by nitrogen. The nickel(II) solution was then added using a syringe, passage of nitrogen was stopped and the polarographic curves were recorded in the dependence on time. When the influence of foreign ions was examined, these ions were added to the reaction mixture using a second syringe simultaneously with nickel(II) ions and similarly as in the previous case the polarographic waves of released cadmium(II) ions were recorded in the dependence of time. The influence of foreign ions on the rate of the studied reaction was also examined using the fixed time method<sup>1</sup> — measurement of the amount of released cadmium(II) ions at the constant time after the start of the reaction, keeping all the reaction conditions constant and varying only the concentration of the foreign ions examined.

## RESULTS

### *Kinetics of Substitution Reactions of Cd-TTHA Chelates with Nickel(II) Ions*

Substitution reactions between the Cd-TTHA chelates and nickel(II) ions were studied under equilibrium conditions<sup>7</sup>, the mechanism of these reactions was established on the basis of kinetic measurements<sup>8</sup>. It has been found that the reaction of mono- and binuclear Cd-TTHA chelates with nickel(II) ions are consecutive reactions with mixed binuclear chelate Cd-Ni-TTHA as reaction intermediate.



In the mechanism expressed by reactions (A) and (B) the rate determining step is the formation of the  $\text{Ni}_2\text{X}^{2-}$  species. Compared with the substitution reactions of the EDTA chelates, where the reaction intermediates are unstable species<sup>9</sup>, the intermediates involved in the substitution reactions of TTHA chelates are stable species, which under specific conditions can be detected polarographically<sup>7,10</sup>.

### *Influence of Foreign Ions on the Substitution Reactions of Cd-TTHA Chelates*

It has been observed that the presence of small concentrations of various metal ions influenced the rate of the substitution reactions (A) and (B). Copper(II) ions showed

the most pronounced effect on the rate of the described reactions. When the initial concentration of the Cd-TTHA chelate was  $5 \cdot 10^{-5} \text{M}$  and that of nickel(II) ions  $5 \cdot 10^{-4} \text{M}$  and reaction (A) was followed in the solution of acetate buffer solution  $\text{pH} = 4.6$ , copper(II) ions influenced the rate of the reaction (A) in a manner as shown on Fig. 1, curve 1. Modifying effect of copper(II) ions depends not only on the amount of copper(II) ions added to the reaction mixture, but also on the concentration of  $\text{H}^+$  ions – see Fig. 1, curves 2 and 3, and on the quality of the buffer solution used. When acetate buffer solution was replaced by ammonia ( $0.2 \text{M}$ ); similar, but no so pronounced modifying effect of copper(II) ions was observed – see Fig. 2, curve 1.

Similarly as in the case of the 1 : 1 Cd-TTHA chelate also the rate of the substitution reaction between the binuclear Cd-TTHA chelate and nickel(II) ions is influenced by the presence of trace concentrations of copper(II) ions – the corresponding dependence is given in Fig. 2, curve 2.

To verify that copper(II) ions only modify the rate of the studied reactions, the possible interactions between the Cd-TTHA chelates and copper(II) ions were examined. Using square wave polarographic technique no released  $\text{Cd}^{2+}$  ions were found in the reaction mixture containing  $\text{CdX}^{2-}$  chelate and copper(II) ions in the molar ratio 1 : 0.1 in the media of acetate buffer and ammonia. When on the other hand, the molar ratio  $[\text{CdX}^{2-}]_0 : [\text{Cu}^{2+}]_0$  was 1 : 5, approx. 15% of the total amount of

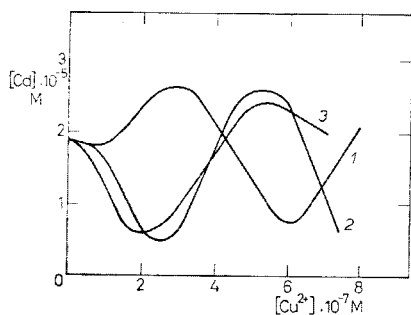


FIG. 1

Influence of  $\text{Cu}^{2+}$  Ions on the Rate of the Reaction (A)

Curves indicate the amount of  $\text{Cd}^{2+}$  ions released after 3 min in the presence of different amounts of  $\text{Cu}^{2+}$  ions.  $[\text{CdX}^{4-}]_0 = 7 \cdot 10^{-5} \text{M}$ ,  $[\text{Ni}^{2+}]_0 = 7 \cdot 10^{-4} \text{M}$ ; acetate and monochloroacetate buffer solutions,  $\text{pH}$  1.4–2, 2.3–5, 3.2–3;  $I = 0.1$ .

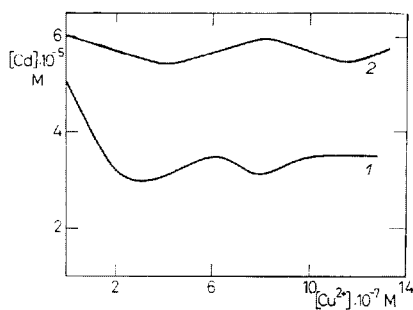


FIG. 2

Influence of  $\text{Cu}^{2+}$  Ions on the Rate of the Reactions (A) and (B) in Ammoniacal Media

Curves indicate the amount of cadmium released after 1.5 min, 2.10 min from the 1 mononuclear, 2 binuclear Cd-TTHA chelate.  $[\text{CdX}^{4-}]_0 = 7 \cdot 10^{-5} \text{M}$ ;  $[\text{Cd}_2\text{X}^{2-}]_0 = 7 \cdot 10^{-5} \text{M}$ ,  $[\text{Ni}^{2+}]_0 = 7 \cdot 10^{-4} \text{M}$ , curve 1  $0.1 \text{M}$  ammonia, curve 2  $0.1 \text{M}$  ammonia +  $0.1 \text{M-NH}_4\text{Cl}$ .

cadmium was set free from the  $\text{CdX}^{2-}$  chelate and simultaneously free copper(II) ions were complexed by the reagent in the amount corresponding approx. to 0.8% of the total amount of cadmium in the system. These findings were obtained by d.c. polarographic measurement of the diffusion current of  $\text{Cd}^{2+}$  ions and by the measurement of the shift of the half-wave potential of the wave of  $\text{Cu}^{2+}$  ions and of the Cu-TTHA chelate<sup>11</sup>. Similar phenomena were observed in the examination of the reaction between the 2 : 1 Cd-TTHA chelate and copper(II) ions, at the reactant ratio  $[\text{Cd}_2\text{X}^{2-}] : [\text{Cu}^{2+}] = 1 : 0.1$ , no released  $\text{Cd}^{2+}$  ions were found, and at the reactant ratio 1 : 5 no nonchelated cadmium(II) ions and also no nonchelated copper(II) ions were observed in the reaction mixture studied.

Using identical technique the effect of  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  ions on the rate of the substitution reaction of Cd-TTHA chelates was examined under identical conditions as described above. The results showed no effect of these metal ions on the rate of studied reaction, when  $\text{Zn}^{2+}$  or  $\text{Co}^{2+}$  ions were present in minor concentrations, molar ratio  $[\text{CdX}^{4-}] : [\text{Zn}^{2+}]$  or  $[\text{Co}^{2+}] = 100 : 1$ . At higher zinc(II) or cobalt(II) ions concentration (molar ratios  $[\text{CdX}^{4-}] : [\text{Zn}^{2+}] = 1 : 0.5$ ), these ions showed no effect on the rate of the studied reactions in slightly acid solution (pH 3–5). On the other hand, an acceleration effect of cobalt(II) and zinc(II) ions on the rate of reaction of Cd-TTHA chelate with nickel(II) ions was observed in amoniacal medium;

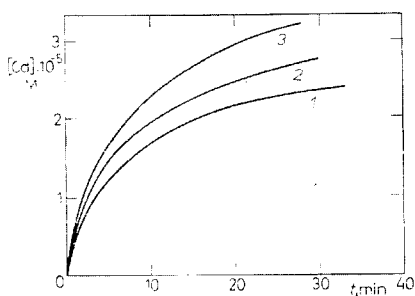


FIG. 3

Influence of  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  Ions on the Rate of the Reaction (A)

Increase of nonchelated  $\text{Cd}^{2+}$  ion concentration in the dependence on time. Curve 1 reaction of  $\text{CdX}^{4-} + \text{Ni}^{2+}$  ions; 2 reaction in the presence of  $\text{Zn}^{2+}$  ions; 3 reaction in the presence of  $\text{Co}^{2+}$  ions;  $[\text{CdX}^{4-}]_0 = 5 \cdot 10^{-5}$ ,  $[\text{Ni}^{2+}]_0 = 5 \cdot 10^{-4}$ ,  $[\text{Zn}^{2+}]_0 = 2.5 \cdot 10^{-5}$ ;  $[\text{Co}^{2+}]_0 = 2.5 \cdot 10^{-5}$  M, reaction medium 0.1 M ammonia.

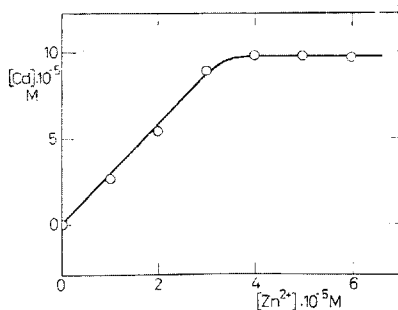


FIG. 4

Influence of  $\text{Zn}^{2+}$  Ions on the Rate of the Reaction (B)

The amount of nonchelated  $\text{Cd}^{2+}$  ions released after 5 min.  $[\text{Cd}_2\text{X}^{2-}]_0 = 5 \cdot 10^{-5}$  M,  $[\text{Ni}^{2+}]_0 = 5 \cdot 10^{-4}$  M, reaction media 0.1 M ammonia and 0.1 M  $\text{NH}_4\text{Cl}$ .

this effect is shown on Fig. 3. The acceleration effect of zinc(II) and cobalt(II) ions is much more pronounced in the reaction of the 2 : 1 Cd-TTHA chelate with nickel ions proceeding in ammoniacal buffer solution, pH 8.2. The rate of this reaction increased with increasing zinc(II) ions concentration, the increase of the rate is however limited as shown on Fig. 4.

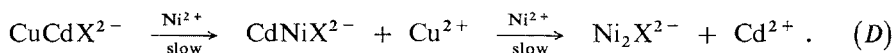
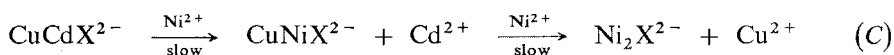
A further examination of the reactions between Cd-TTHA chelates and zinc(II) or cobalt(II) ions showed, that in ammoniacal solutions both these ions present in excess compared to the conc. of  $\text{CdX}^{4-}$  chelate released such molar amount of  $\text{Cd}^{2+}$  ion from the cadmium(II) chelate which is equal to the amount of zinc(II) ions (or cobalt(II)) transferred simultaneously from the corresponding ammonia complexes to the TTHA chelates. These findings follow from the measurement of the decrease of the wave heights of cobalt(II) or zinc(II) in ammoniacal media, where the corresponding TTHA chelates are not polarographically active. Examination of the reaction of the 2 : 1 Cd-TTHA chelate with an excess of zinc(II) or cobalt(II) ions showed that a fraction (approx. 15%) of cadmium(II) ions from the chelate was set free and simultaneously the concentration of nonchelated zinc(II) or cobalt(II) ions decreased. This decrease is however 3 times higher than corresponds to the release of cadmium(II) ions under identical conditions.

## DISCUSSION

The results given here show the effects of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  ions on the rate of substitution reactions of the Cd-TTHA chelates with nickel(II) ions. A rather unique effect was observed in the case of the copper(II) ions, when these ions were present in trace concentrations in the studied reaction system. These ions were found either to accelerate or to inhibit the rate of the studied substitution reaction. On the other hand, cobalt(II) or zinc(II) ions showed only rate accelerating effects on the same reaction.

On the basis of the experimental results given above, acceleration effects of zinc(II) or cobalt(II) ions are to be expected. Acceleration effect of these ions can be observed only when higher concentrations of zinc(II) or cobalt(II) ions are present in the reaction mixture. Under these conditions, zinc(II) and cobalt(II) ions caused a release of  $\text{Cd}^{2+}$  ions from the Cd-TTHA chelates, the corresponding substitution reactions are accompanied with the formation of mixed binuclear chelates  $\text{CdZnX}^{2-}$  and  $\text{CdCoX}^{2-}$  respectively, reaction of these mixed chelates with an excess of nickel(II) ions lead to the formation of the more stable  $\text{Ni}_2\text{X}^{2-}$  chelate<sup>7</sup>. The increase of the rate of the reaction between Cd-TTHA chelates and nickel(II) ions is therefore to be expected when moderate amounts of zinc(II) or cobalt(II) ions are added to the reaction mixture. In the presence of trace amounts of zinc(II) or cobalt(II) ions no acceleration can be observed due to the minimum rate of the reactions between the Cd-TTHA chelates and zinc(II) or cobalt(II) ions.

The modifying effect of copper(II) ions is, on the other hand, of another type because these ions alter the reaction rate at their very low concentration (molar ratio  $[\text{CdX}^{4-}]/[\text{Cu}^{2+}] = 200$  and more). The acceleration of the reaction rate cannot be attributed to the exchange of cadmium(II) ions from the chelate by copper(II) ions under the given conditions. From the data based on the measurement of the increase of the free cadmium(II) ions concentration during the course of the reaction between Cd-TTHA chelate and nickel(II) ions in the presence of trace amounts of copper(II) ions it cannot be distinguished if copper(II) ions influence only the first step (formation of the mixed binuclear chelate) of the reaction (A) and (B) or only the second reaction step (reaction of the mixed chelate with nickel(II) ions). The experiments carried out with Cd-TTHA chelates and only copper(II) ions showed, however, the decrease of the concentration of nonchelated  $\text{Cu}^{2+}$  ions which is not proportional to the amount of cadmium(II) ions released from the TTHA chelate – in the case of the reaction of the 1 : 1 cadmium chelate. This finding indicates that the formation of the mixed binuclear chelate  $\text{CuCdX}^{2-}$  must also be considered. The formation of this mixed binuclear chelate in the reaction between the Cd-TTHA chelates and copper(II) ions is relatively fast, because no time dependence was observed in the corresponding experiments. If the 1 : 1 and the 2 : 1 cadmium chelates react with  $\text{Cu}^{2+}$  ions forming the  $\text{CuCdX}^{2-}$  species in a rapid step at the beginning of the reaction, the substitution reaction studied can proceed according to following two reaction paths



As all, up to now known mixed binuclear chelates of TTHA reagent, also the  $\text{CuCdX}^{2-}$  chelate is formed in a fast reaction and its stability must be smaller than the stability of the simple cadmium(II) or nickel(II) TTHA chelates. Therefore, in the presence of an excess of  $\text{Ni}^{2+}$  ions, the formation of  $\text{CuNiX}^{2-}$  and/or  $\text{CdNiX}^{2-}$  chelates must occur as shown in the proposed reaction scheme ((C), (D)). Simultaneous exchange of two metal atoms from a binuclear TTHA was not observed; in all cases studied up to now, the substitution process occurred in two steps. Which of the reaction paths (C) and (D) prevails in the system depends probably on the relative amount of the Cd-TTHA chelate and copper(II) and nickel(II) ions. The existence of the both mixed binuclear chelates Cu-Ni-TTHA and Cd-Ni-TTHA has already been proven<sup>7,11</sup>, the corresponding equilibrium constants  $K_{\text{CuNiX}}^{\text{Cu}}$  and  $K_{\text{CdNiX}}^{\text{Cu}}$  have the log values 15.3 and 9.2 respectively. A mixed binuclear chelate containing one nickel atom reacts then with nickel(II) ions present in the solution, this reaction results in the formation of the stable product  $\text{Ni}_2\text{X}^{2-}$ .

From the reaction scheme ((C), (D)) it follows, that under the conditions, where the reaction rate is determined by the measurement of the increase of the concentration of nonchelated cadmium(II) ions in the dependence of time, the obtained results will indicate a higher rate when the mixed binuclear chelate  $\text{CuNiX}^{2-}$  is predominately formed and a lower rate, when only  $\text{CdNiX}^{2-}$  chelate is formed. This statement is correct under the validity of an acceptable assumption that the rates of the reactions of mixed binuclear chelates are slow and do not differ too much. In both cases of reaction scheme ((C), (D)), copper(II) ions remain unaltered at the end of the reaction cycle and formally can be considered as catalyst. Experimentally, using the polarographic technique, the presence of free copper(II) ions can be detected when the main (indicator) reaction reaches completion.

The proposed reaction mechanism is supported by the following experimental finding. The curves expressing the time dependence of the concentration of released cadmium(II) ions during the course of the indicator reaction in the presence of copper(II) ions show some irregularities at the beginning of the reaction. This phenomenon can be explained by the existence of induction period, which follows from the reaction scheme (D) (no cadmium(II) ions are set free during the first two reaction steps). Induction period is, however, masked by the course of the reaction of the larger fraction of the Cd-TTHA chelate with nickel(II) ions in excess and therefore no distinguished induction period can be detected in the reaction system described.

Quantitative interpretation of the described phenomena cannot be given on the basis of obtained experimental data. For detailed explanation more experimental data based on the measurement of fast reaction are necessary.

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