

MULTIDENTATE LIGAND KINETICS:
REACTION OF NICKEL(II) WITH COPPER CHELATES
OF TRIETHYLENETETRAMINEHEXAACETIC ACID

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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The kinetics of the substitution reaction between hydrated nickel(II) ions and copper-triethylenetetraminehexaacetate was studied in the pH interval from 2 to 5.5. It was found that the deprotonized binuclear copper chelate reacts with nickel(II) ions; the first step of the reaction is the fast formation of the mixed binuclear chelate CuNiX^{2-} . The rate determining step is the formation of the binuclear nickel chelate. The mixed binuclear chelate is also formed during the reverse reaction; the attack of copper(II) ions on the mixed binuclear chelate is faster.

Substitution reactions involving the chelates of EDTA and related compounds have been extensively studied by various authors^{1,2}. Recently great interest has been paid to the study of the kinetics and mechanism of these reactions; for kinetic measurements, mostly spectrophotometry³⁻⁶ and polarography⁷⁻¹⁰ were applied.

The study of the reactions of copper(II) ions with the nickel chelate of EDTA¹¹ or HEEDTA³ (*i.e.* N-hydroxyethylenediaminetriacetic acid) has shown that mixed binuclear chelates Cu-Ni-L are formed as relatively stable reaction intermediates. On the other hand, in the substitution reaction of copper(II) ions with the nickel chelate of DCTA⁴ (*i.e.* *trans*-1,2-diaminocyclohexane-N,N,N',N'tetraacetic acid) the cyclohexane ring prevents the full rotation of the two iminodiacetate segments of the ligand and the formation of mixed binuclear chelate is not possible.

This study presents the results of the investigation of the kinetics of the reaction between nickel(II) ions and copper chelate of triethylenetetraminehexaacetic acid (TTHA or H_6X). The TTHA reagent, introduced by Frost¹², has ten coordinating centers and is able to form mono- and binuclear chelates¹³⁻¹⁶ with various metal ions. The system studied in this work is expressed by the reactions



and



Recently, the system containing copper(II) and nickel(II) ions and TTHA reagent was examined under equilibrium conditions¹⁷ and it has been found that the mixed binuclear chelate Ni-Cu-TTHA may be formed under certain conditions.

EXPERIMENTAL

Reagents and apparatus. THHA solution was prepared from R. G. chemical (Dojin Pharmaceutical Laboratories, Japan) and standardized by amperometric titration with a zinc solution. Solutions of nickel(II) chloride were prepared from R. G. chemical (E. Merck, Darmstadt); the solution of copper(II) nitrate was prepared by dissolution of R. G. copper metal. Both solutions were standardized by EDTA titrations. Other solutions used were prepared from R. G. chemicals. Sodium perchlorate was used to adjust the ionic strength of all solutions. Spectrophotometric measurements were carried out using the spectrophotometer Unicam SP/800 (Unicam Instr., England) with a thermostated cell compartment; pH values of the solutions examined were measured with the Radiometer pH meter PHM-25 and a glass electrode.

Procedure. The rate of the reactions (A) and (B) was studied in a sodium perchlorate medium in the pH interval from 2 to 6. Copper hydrolysis should not be appreciable in the pH range below pH 5.5. The rate of the reactions studied was followed by the spectrophotometric measurement at the absorption bands of mono- and binuclear copper-TTHA chelates. The 1 : 1 copper-TTHA chelate yields absorbance maxima at 710^{15,18} and 260 nm at pH 4.7; the 2 : 1 chelate yields maxima at practically identical wave lengths¹⁸ under identical conditions. The values of the molar extinction coefficients at pH 4.7 and at the wave lengths 710 and 260 nm are 74 (ref.¹⁸) and 3600 resp. for the 1 : 1 chelate, and 135 (ref.¹⁸) and 6300 resp. for the 2 : 1 chelate. Spectra of the 1 : 1 and 2 : 1 copper-TTHA chelates together with the changing spectra of the 2 : 1 copper chelate during the reaction with nickel(II) ions are shown in Fig. 1. For the determination of the concentration of the copper chelate in the presence of nickel(II) ions, the measurement in the UV region is more convenient because nickel exhibits absorption maxima at approximately 720 nm, while in the UV region 260 nm no absorbance maxima due to the presence of nickel ions or the nickel-TTHA chelate were found. The values for molar extinction coefficients of free copper(II) and free nickel(II) ions and of nickel-TTHA chelates have values less than 10 at the wave length 260 nm. The concentration of the 1 : 1 copper-TTHA chelate was calculated according to the expression

$$[\text{CuX}]' = (A_0 - A)/b(\epsilon_{\text{Cu}_2\text{X}} + \epsilon_{\text{Ni}} - \epsilon_{\text{Ni}_2\text{X}} - \epsilon_{\text{Cu}}), \quad (1)$$

where $[\text{CuX}]'$ is the sum of all protonated and unprotonated forms of Cu-TTHA chelate at any time, b is the cell length, A is the absorbance observed at the time t and A_0 is the initial absorbance at zero time. The concentration of the 2 : 1 copper chelate was calculated according to an expression similar to equation (1).

RESULTS

Kinetics of the Reaction of the Cu_2X^{2-} Chelate with Nickel(II) Ions

Due to the relatively large difference between the values of the stability constants of the 2 : 1 and 1 : 1 copper-TTHA chelates ($\log \beta_{\text{Cu}_2\text{X}} = 32.6$; $\log K_{\text{CuX}}^{\text{Cu}} = 19.1$)¹⁵, the existence of only Cu_2X^{2-} species can be supposed in a solution containing copper(II) ions and TTHA reagent in the molar ratio 2 : 1. Polarographic measurements described by Haque¹⁷ verified this proposal. From the detailed study published by Harju and Ringbom^{15,19}, it follows that, when the system contains copper ions and TTHA reagent in the molar ratio 2 : 1, some amount of the 1 : 1 copper chelate is formed even in acidic medium. This amount is very small and cannot influence sufficiently the reaction studied in the given pH interval.



The formation of 1 : 1 chelate must be, however, taken into consideration, when equilibrium (stability) constants of the species involved are to be determined. After the addition of nickel(II) ions to the solution of the 2 : 1 copper chelate the course of the reaction (A) was examined. The spectrophotometric data showed that the reaction (A) proceeds in the right hand direction only in the presence of a large excess of nickel(II) ions. The addition of nickel salt to the solution of Cu_2X^{2-} chelate changed the shape of the absorbance curve immediately, as shown in Fig. 1. The new absorbance curves (Fig. 1, curves 3, 4) reminded the curves of the binuclear chelate, a more detailed examination showed, however, that these curves were not identical. The proposal was therefore made that the new absorbance curves corresponded to the existence of the mixed binuclear chelate CuNiX^{2-} , formed immediately after mixing of the reactants. Under the conditions (50–500 times excess of nickel(II) ions over the concentration of Cu_2X^{2-} chelate, ionic strength equal to 0.2) the plot of the reciprocal value of $[\text{CuNiX}^{2-}]$ vs. time gave a linear dependence, showing thus the pseudo-second order of the reaction studied. During these experiments it has been observed that the value of the intercept at the ordinate of this line corresponding to zero time was not equal to the theoretical value $1/[\text{Cu}_2\text{X}^{2-}]_0$. The experimental value was higher in all measurements carried out under various conditions (pH and concentration of the reactants).

The values of the pseudo-second order rate constant k_0 are summarized in Table I. The results of the experiments presented in Table I show that the rate of the reaction studied is not influenced by pH in the interval from 3 to 5.5. The dependence of the log value of the rate constant k_0 on the logarithm of nickel(II) ion concentration gave a line with a slope equal to 0.49. According to this dependence, the following relation between the pseudo-second order rate constant k_0 and nickel(II) ions concentration should be valid

$$k_r = k_0/[\text{Ni}^{2+}]^{0.5} \quad (2)$$

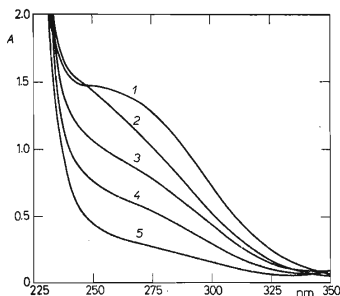


FIG. 1

Absorption Spectra of the Reaction between Copper-TTHA Chelates and Nickel(II)

1 1 : 1 copper chelate; $[\text{CuX}^{4-}]_0 = 4 \cdot 10^{-4} \text{ M}$;
2 2 : 1 copper chelate; $[\text{Cu}_2\text{X}^{2-}]_0 = 2 \cdot 10^{-4} \text{ M}$; 3–5 time course of the reaction studied; $[\text{Cu}_2\text{X}^{2-}]_0 = 10^{-4} \text{ M}$; $C_{\text{Ni}} = 0.1 \text{ M}$; 1.5; 10 and 40 min after mixing; pH 3.5; cell length 10 mm, 27°C; $\mu = 0.2$.

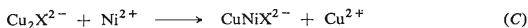
TABLE I

Rate Constant for Nickel Attack on $\text{Cu}_2\text{-TTHA}$ Chelate
 $\mu = 0.2, 27^\circ\text{C}$.

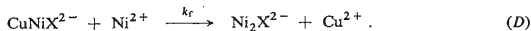
$[\text{Cu}_2\text{X}]_0 \cdot 10^4$ mol l^{-1}	pH	C_{Ni} mol l^{-1}	$k_0 \cdot 10^{-2}$ $\text{l mol}^{-1} \text{s}^{-1}$	$k_f \cdot 10^{-2}$ $\text{l}^{3/2} \text{mol}^{-3/2} \text{s}^{-1}$
2.0	3.25	0.05	2.08	9.30
2.0	4.40	0.05	2.08	9.30
2.0	4.40	0.10	2.97	9.40
2.0	4.70	0.025	1.43	9.09
2.0	5.50	0.05	2.06	9.21
3.0	3.25	0.15	3.59	9.30
3.0	4.70	0.037	1.73	9.01
3.0	5.50	0.06	2.38	9.71
4.0	3.25	0.02	1.32	9.36
4.0	4.40	0.04	1.99	9.95
4.0	5.50	0.08	2.66	9.43
4.0	2.50	0.04	1.04	5.15

and the ratio $k_0/[\text{Ni}^{2+}]^{0.5}$ should be constant. From the data presented in Table I it is evident that the ratio is in fact constant in the pH interval from pH 3 to pH 5.5 and at various initial concentrations of Cu_2X^{2-} chelate.

The finding given above, together with the results of the earlier work¹⁷, led to the proposal that the first step of the reaction (A) is the rapid formation of the binuclear mixed chelate NiCuX^{2-} according to the reaction



and the rate determining step is the formation of the products according to the reaction



According to the results described, the rate of the reaction studied can be expressed as

$$d[\text{Ni}_2\text{X}^{4-}]/dt = k_0[\text{CuNiX}^{2-}]^2 = k_f[\text{CuNiX}^{2-}]^2 [\text{Ni}^{2+}]^{0.5}, \quad (3)$$

where k_f is defined by equation (2).

The authors were not able to find any theoretical explanation of the somewhat unusual form of the rate equation (3). Up to now, half order dependence was not determined in the study of the kinetics of the substitution reactions involving the chelates of EDTA type³⁻⁵.

Kinetics of the Reaction of the CuX^{4-} Chelate with Nickel(II) Ions

As mentioned above, the formation of either 1 : 1 or 2 : 1 TTHA chelates depends on the ratio metal/ ion ligand and on pH^{19} . In the system copper-TTHA it is practically impossible to prepare a solution containing only CuX^{4-} chelate. Therefore in further kinetic measurements carried out with equimolar mixture of copper and TTHA, the formation of Cu_2X^{2-} chelate was considered.

The spectrophotometric measurements with 1 : 1 molar mixture of copper(II) ions and TTHA reagent gave practically identical results as in the case of the reaction of the binuclear copper chelate with nickel(II) ions. In the presence of an excess of nickel(II) ions reaction studied showed pseudo second order dependence; the values of the corresponding rate constants are summarized in Table II. As in the previous case, the dependence of the log value of the observed pseudo second order constant k'_0 on the logarithm of the nickel(II) ion concentration can be represented by a line with a slope equal to 0.53.

Kinetics of the Reverse Reaction

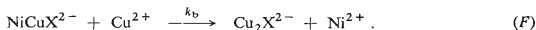
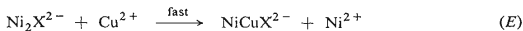
The reverse reaction (interaction between the 2 : 1 nickel-TTHA chelate with copper(II) ions) was studied in the pH interval 3–5.5 and at the ionic strength 0.2. As mentioned above, the nickel-TTHA chelates produce no absorbance maxima in the UV region. This means that the concentration of the Cu_2X^{2-} chelate formed during the course of the reverse reaction (A) could be measured spectrophotometrically. On the other hand it was observed that the solution containing copper(II) and nickel(II) ions and the reagent in the molar ratio 1 : 1 : 1 produced an absorbance maximum. The shape of this maximum was practically identical with that of the 2 : 1 copper-TTHA chelate but with half the absorbance. It was therefore supposed that this maximum was due to the presence of the mixed binuclear chelate NiCuX^{2-} in the solution examined.

TABLE II

Rate Constant for Nickel Attack on Cu-TTHA Chelate
 $\mu = 0.2$; 27°C.

$[\text{CuX}]_0 \cdot 10^4$ mol l^{-1}	pH	C_{Ni} mol l^{-1}	$k'_0 \cdot 10^{-2}$ $\text{l mol}^{-1} \text{s}^{-1}$	$k'_f \cdot 10^{-2}$ $\text{l}^{3/2} \text{mol}^{-3/2} \text{s}^{-1}$
2.0	2.5	0.10	3.60	11.4
2.0	3.5	0.02	1.37	9.72
4.0	3.5	0.20	3.80	8.55
4.0	4.5	0.04	1.75	8.75
8.0	3.5	0.20	2.90	6.50
8.0	5.0	0.40	4.50	7.20

During the examination of the reverse reaction it was observed that after the addition of the copper(II) salt into the solution of the 2 : 1 nickel chelate, the absorbance at 260 nm immediately increased and subsequently changed only little with time. This phenomenon was explained as follows: After the addition of copper(II) ions to the solution of Ni_2X^{2-} chelate, the mixed binuclear chelate NiCuX^{2-} was formed in a fast reaction. The binuclear chelate was further transformed to the Cu_2X^{2-} chelate as shown by the reactions:



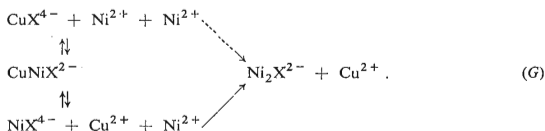
It is evident that during the course of the reaction (F), the concentration of Cu_2X^{2-} chelate increases with time while the concentration of the mixed binuclear chelate decreases. Because the absorbance the Cu_2X^{2-} chelate is equal to two times the absorbance of an identical concentration of the mixed NiCuX^{2-} chelate, the approximate concentration of the CuNiX^{2-} chelate was determined spectrophotometrically using the data measured at two different times. The difference in the measured absorbance is due to the decrease of CuNiX^{2-} concentration (equal to $-a$ units) and to the increase of Cu_2X^{2-} concentration (equal to $+2a$ units). Using the data thus calculated the concentration-time curve was constructed for the reverse reaction and it was found that this reaction under identical conditions (pH, excess of copper(II) ions) is approx. 10–15 times faster than the forward reaction.

DISCUSSION

The examination of the kinetics of the reaction between the Cu_2X^{2-} chelate and nickel(II) ions showed that the reaction rate was pH independent in the range from 3 to 5.5. This finding led to the conclusion that the reacting species is only Cu_2X^{2-} in the given pH region. This agrees very well with the results of Harju¹⁵, who, using potentiometric measurements, found that the protonated binuclear copper chelate existed only at pH values below 3.

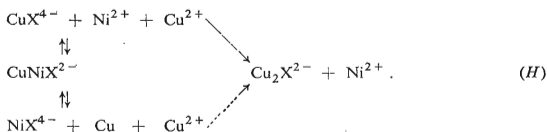
The electrophilic substitution reaction as examined throughout this work must involve some reaction intermediate, where two metal ions are coordinated to one TTHA molecule, as has been observed in the study of the substitution reaction of complexes of EDTA and other multidentate ligands^{3–8}. In the case of the reaction between the Ni-EDTA chelate and copper(II) ions, the intermediate concentration is not appreciable compared with the total concentration of the reactants and products¹¹. On the other hand, in the reaction of the binuclear copper-TTHA chelate with nickel(II) ions, the mixed binuclear chelate CuNiX^{2-} is formed immediately in measurable concentrations. The formation of the mixed binuclear chelate under equilibrium conditions was recently verified and the corresponding equilibrium constant $K_{\text{CuNiX}}^{\text{Cu}}$ was determined¹⁷. The difference between the formation of the mixed binuclear chelates of EDTA and TTHA are evidently due to the different structures of these reagents; TTHA has ten coordinating centers and has full ability to form binuclear chelates.

The attack of nickel(II) ions on the mixed binuclear chelate (reaction (D)) results in the formation of the binuclear nickel-TTHA chelate and the release of copper(II)-ions. It can be supposed that the mixed binuclear chelate CuNiX^{2-} is in a mobile equilibrium with free nickel(II) ions and the 1 : 1 copper-TTHA chelate and also with free copper(II) ions and the 1 : 1 nickel-TTHA chelate. The system studied may be expressed in simplified form by the reaction scheme:



Because nickel(II) ions are present in a large excess compared with the concentration of the mixed binuclear chelate, the formation of the CuX^{4-} chelate during establishment of the mobile equilibrium on the left-hand side of reaction (G), will be suppressed and the formation of the resulting Ni_2X^{2-} chelate will proceed mostly by the addition of nickel to the NiX^{4-} chelate.

In the presence of a large excess of copper(II) ions over the concentration of Ni_2X^{2-} chelate, reaction (H) may explain the mechanism of the reverse reaction



In the first, fast step the mixed binuclear chelate is formed and an excess of copper(II) ions in the system causes the formation of the Cu_2X^{2-} chelate.

The value of the equilibrium constant of the reaction (D), defined as

$$K_D = [\text{Ni}_2\text{X}^{2-}] [\text{Cu}^{2+}] / [\text{CuNiX}^{2-}] [\text{Ni}^{2+}] = K_{\text{Ni}_2\text{X}}^{\text{Ni}} / K_{\text{CuNiX}}^{\text{Cu}} \quad (4)$$

may be calculated, since the stability constants of the Ni_2X^{2-} chelate $K_{\text{Ni}_2\text{X}}^{\text{Ni}}$ (reaction: $\text{NiX}^{4-} + \text{Ni}^{2+} \rightleftharpoons \text{Ni}_2\text{X}^{2-}$) and the equilibrium constant of the CuNiX^{2-} chelate $K_{\text{CuNiX}}^{\text{Cu}}$ (reaction: $\text{NiX}^{4-} + \text{Cu}^{2+} \rightleftharpoons \text{CuNiX}^{2-}$) are known^{15,17}. The value of the equilibrium constant K_D was calculated to be 10^{-1} , using the values: $\log K_{\text{Ni}_2\text{X}}^{\text{Ni}} = 14.3$ (ref.¹⁵) and $\log K_{\text{CuNiX}}^{\text{Cu}} = 15.3$ (ref.¹⁷). The value of the forward rate constant k_f (corresponding to the reaction (D)) was found in this work to be $9.3 \cdot 10^2 \text{ l}^{3/2} \text{ mol}^{-3/2} \text{ s}^{-1}$; the value of the corresponding rate constant k_b of the reverse reaction was calculated to be $9.3 \cdot 10^3 \text{ l}^{3/2} \text{ mol}^{-3/2} \text{ s}^{-1}$ using the expression $K_D = k_f/k_b$.

This value is acceptable, because it does not disagree with the general theory that copper(II) would be expected to be a more effective electrophilic agent than nickel(II), if they proceeds through the same intermediate¹¹.

As stated in the experimental part of this work, practically identical results were obtained in the kinetic study of the reaction of 1 : 1 copper-TTHA chelate with nickel(II) ions. This finding is to be expected because at pH values around 4, the binuclear copper-TTHA chelate predominates in the system in which the molar ratio of copper(II) to the ligand is 1 : 1, as has been calculated¹⁵ and experimentally proved¹⁷.

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