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# Central Atom Exchange Reactions in Complexes with Tetradentate Thioiminato Schiff Base Ligand

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*The kinetics of central atom exchange reactions between the quasi-square-planar Schiff base thioiminato-complexes of Zn(II) and $Ni^{2+}$ ion has been studied. It has been found that the second-order rate constants of the reactions increase with increasing electron density localized on the chromophore of the complexes. The experimental data indicate that the investigated reactions proceed through a dinuclear intermediate whose formation is the rate-determining step of the reactions. The electrophilic character of the studied substitution reactions was proved.*

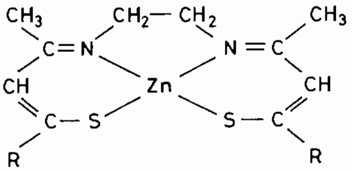
## Introduction

Electrophilic central atom exchange reactions were investigated especially in complexes with tetradentate ligands of the porphyrin type [1] and with aminocarboxylate ligands [2]. The study was directed to the mechanisms and the steric influence effects on the reaction kinetics. The authors of paper [3] studied the relationship between the electronic properties of the ligand, coordinated in the equatorial plane of the complex, and the kinetics of the exchange reaction of central atoms. Based on the study of the exchange reaction rate of Zn(II) for Cu(II) in Zn(X–P) complexes, where X–P denotes substituted porphyrin derivatives, the cited paper concluded that the rate determining factor of the reactions, involving formation and decomposition of an intermediate with the entering and the leaving central atoms coordinated to the macrocyclic ligand, was the break of Zn–N bonds, but not the formation of Cu–N bonds. Namely, the greater the electron density on the nitrogen donor atoms (due to substituents on the porphyrin ring), the slower was the reaction course.

Continuing our studies of electronic structure [4, 5], electrochemical properties [6–8], and preparation [9] of some complexes with ethylenebis/thioacetylacetoniminato/ligand and its derivatives, selected as model compounds for studying the consequences of equatorial-axial effects [10], the exchange reactions of the central atom Zn(II) for Ni(II) were investigated:

$$ZnN_2S_2R_2 + Ni^{2+} = NiN_2S_2R_2 + Zn^{2+} \qquad (1)$$

in complexes:



R = $CH_3$; $CF_3$; $C_6H_5$; 4-Cl-$C_6H_4$; 4-Br-$C_6H_4$; 4-$CH_3O$-$C_6H_4$;

further on denoted as $ZnN_2S_2R_2$.

The aim of the present study was to establish the mechanism of the reactions (1) based on investigation of the reaction kinetics, and to elucidate the influence of the electronic properties of the $N_2S_2R_2^{2-}$ ligand (determined by the properties of the substituent R) on the rate constants of the studied reactions.

## Experimental

The complex $ZnN_2S_2(CH_3)_2$ was prepared according to [11], the ligands $H_2N_2S_2R_2$ (R = $CF_3$; $C_6H_5$; 4-Cl-$C_6H_4$; 4-Br-$C_6H_4$; and 4-$CH_3O$-$C_6H_4$) were prepared and characterized by elemental analysis, IR and NMR spectroscopy [9] (full information concerning the preparation and characterization of the ligands as well as some complexes of the ligands will be published separately [9]). $Ni(py)_4Cl_2$ compound (py = pyridine) was kindly rendered by Dr. Jamnický; $Ni^{2+}$ content was determined chelatometrically. Water-free $ZnCl_2$ p.a. (Lachema) was not

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TABLE I. Dependence of the Rate of Reaction (2), v, on the Concentration of $Ni^{2+}$ Ion at the Time of Reaction t = 0. Concentrations of $[ZnN_2S_2(CH_3)_2]$ = 6.57 × $10^{-5}$ *M*; $[ZnCl_2]$ = 1.0 × $10^{-3}$ *M*; Solvent Methanol, Temperature 15.0 ± 0.1 °C.

| $[Ni^{2+}] \times 10^5$, *M* | $v \times 10^5$, *M* $min^{-1}$ |
|---|---|
| 1.5 | 0.333 |
| 3.0 | 0.612 |
| 4.5 | 0.777 |
| 6.0 | 1.110 |
| 7.5 | 1.270 |
| 9.0 | 1.550 |
| 10.5 | 1.800 |
| 12.0 | 2.000 |
| 13.5 | 2.610 |
| 15.0 | 2.770 |

TABLE II. Dependence of the Rate of Reaction (2), v, on the Concentration of $ZnN_2S_2(CH_3)_2$ Complex at the Time of Reaction t = 0. Concentration of Ion $[Ni^{2+}]$ = 1.0 × $10^{-4}$ *M*; $[ZnCl_2]$ = 1.0 × $10^{-3}$ *M*; Solvent Methanol, Temperature 15.0 ± 0.1 °C.

| $[ZnN_2S_2(CH_3)_2] \times 10^5$, *M* | $v \times 10^5$, *M* $min^{-1}$ |
|---|---|
| 1.33 | 0.38 |
| 2.67 | 0.89 |
| 4.00 | 1.16 |
| 5.33 | 1.54 |
| 6.67 | 2.05 |
| 8.00 | 2.31 |
| 9.33 | 2.56 |
| 10.67 | 3.08 |

adapted before use. Methanol p.a. (Lachema) was dried over $Mg(OCH_3)_2$ and then distilled.

Solutions of $ZnN_2S_2R_2$ were prepared by dissolving a weighted amount of the ligand in 2 × $10^{-3}$ *M* $ZnCl_2$ in methanol.

The reaction course was followed spectrophotometrically. The values of the rate constants k were obtained by evaluating the time dependences of absorbances A for systems with selected started ratios of $[ZnN_2S_2R_2]:[Ni^{2+}]$. The wavelengths were chosen in such a way that the differences between the molar absorption coefficients of $ZnN_2S_2R_2$ and $NiN_2S_2R_2$ complexes should be the greatest possible and the absorbance by solvated $Zn^{2+}$ and $Ni^{2+}$ ions should be negligible.

During the preparation and the measurements the solutions were kept in the dark and under argon atmosphere, at a temperature of 15.0 ± 0.1 °C. In order to ensure a constant ionic strength and to suppress some potential dissociation of $ZnN_2S_2R_2$ complexes, the started solutions (prepared by mixing the solution of $ZnN_2S_2R_2$ complex containing $ZnCl_2$ with solution of $Ni(py)_4Cl_2$ in methanol and with methanol) contained $ZnCl_2$ of the concentration 1.0 × $10^{-3}$ *M*.

## Results

The rate of the reaction

$$ZnN_2S_2(CH_3)_2 + Ni^{2+} = NiN_2S_2(CH_3)_2 + Zn^{2+} \qquad (2)$$

was studied in the systems with constant starting concentrations of $[ZnN_2S_2(CH_3)_2]$ = 6.57 × $10^{-5}$ *M* and of $[ZnCl_2]$ = 1.0 × $10^{-3}$ *M*; and with $Ni(py)_4Cl_2$ (further on $Ni^{2+}$) concentrations in the range of 1.5 × $10^{-5}$ *M* to 1.5 × $10^{-4}$ *M* at 333 nm, where $\epsilon_{[ZnN_2S_2(CH_3)_2]} = 7000\ M^{-1}\ cm^{-1}$ and $\epsilon_{[NiN_2S_2(CH_3)_2]} = 3850\ M^{-1}\ cm^{-1}$. From the dependences of $A_{333}$ on time in the time t = 0 it follows that the rate of reaction, v, calculated using equation (3)

$$v = \frac{d[NiN_2S_2(CH_3)_2]}{dt} = \frac{dA/dt}{l[\epsilon_{[NiN_2S_2(CH_3)_2]} - \epsilon_{[ZnN_2S_2(CH_3)_2]}]} \qquad (3)$$

is linearly proportional to the concentration of $Ni^{2+}$ ions (Table I). Analogically, in following the spectral changes at 426 nm ($\epsilon_{[NiN_2S_2(CH_3)_2]} = 2500\ M^{-1}\ cm^{-1}$ and $\epsilon_{[ZnN_2S_2(CH_3)_2]} = 0$) in systems with constant $Ni^{2+}$ concentration of 1.0 × $10^{-4}$ *M* and $[ZnCl_2]$ = 1.0 × $10^{-3}$ *M*; and with concentrations of $ZnN_2S_2(CH_3)_2$ complex in the range of 1.33 × $10^{-5}$ *M* to 1.06 × $10^{-4}$ *M* (Table II) it was found that the reaction rate was linearly proportional to the concentration of $ZnN_2S_2(CH_3)_2$ complex. The experimental rate law is therefore:

$$v = k[ZnN_2S_2(CH_3)_2]\,[Ni^{2+}] \qquad (4)$$

From the data in Table I the value of the rate constant k = 2750 ± 60 $M^{-1}$ $min^{-1}$, while from those in Table II, the value of k = 2880 ± 45 $M^{-1}$ $min^{-1}$ was obtained, the mean value being k = 2815 $M^{-1}$ $min^{-1}$; the differences in k values can be a consequence of the inaccurate determination of the molar extinction coefficient values.

Study of the spectral changes of systems with initial constant concentrations of $[Ni^{2+}]$ = 1.0 × $10^{-4}$ *M* and $[ZnN_2S_2(CH_3)_2]$ = 8.0 × $10^{-5}$ *M* not containing $ZnCl_2$ (prepared by dissolving the solid $ZnN_2S_2(CH_3)_2$ complex in methanol) and of systems with $ZnCl_2$ concentrations of 2.0 × $10^{-4}$ *M*;

TABLE III. Values of Wavelengths λ at which the Course of Reactions (2) was followed, Molar Absorption Coefficients of the Complexes at given λ, Second-Order Rate Constants k, and Taft's Parameters σ in Dependence on R.

| R | λ nm | $\epsilon_{(NiN_2S_2R_2)}$ $M^{-1}$ $cm^{-1}$ | $\epsilon_{(ZnN_2S_2R_2)}$ $M^{-1}$ $cm^{-1}$ | k $M^{-1}$ $min^{-1}$ | σ |
|---|---|---|---|---|---|
| $CF_3$ | 435 | 1050 | 0 | 702 ± 12 | 2.50 |
| $4\text{-Br-}C_6H_4$ | 355 | 16900 | 38100 | 6320 ± 250 | 0.83 |
| $4\text{-Cl-}C_6H_4$ | 358 | 12800 | 35300 | 6600 ± 160 | 0.83 |
| $C_6H_5$ | 340 | 7700 | 47700 | 7070 ± 250 | 0.60 |
| $4\text{-}CH_3O\text{-}C_6H_4$ | 355 | 25000 | 45500 | 9910 ± 380 | 0.33 |

$6.0 \times 10^{-4}$ $M$ and $1.0 \times 10^{-3}$ $M$ showed that in the given concentration range, $ZnCl_2$ does not influence the reaction rate of the studied exchange reaction.

As the spectral measurements in UV and visible region showed, the exchange reaction (2) runs quantitatively; the spectra of the systems are a superposition of the spectra of $ZnN_2S_2(CH_3)_2$ and $NiN_2S_2(CH_3)_2$ complexes and they exhibit an isosbestic point at 392 nm.

The exchange reactions in systems with the other Zn(II) complexes were investigated analogically as in the case of reaction (2). The experimental measuring conditions (wavelength values at which the reaction course was followed and the values of molar absorption coefficients at a given wavelength for complexes) as well as the computed values of the rate constants k are listed in Table III.

## Discussion

In concordance with the literature, on the basis of obtained experimental data, the following mechanism for the studied reactions may be postulated:

$$ZnN_2S_2R_2 + Ni^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \{Zn(N_2S_2R_2)Ni\}^{2+} \xrightarrow{k_3} Zn^{2+} + NiN_2S_2R_2 \qquad (5)$$

In the first step (process characterized by the rate constant $k_1$) the formation of an intermediate takes place, which is formed from tetradentate ligand and from the leaving and the entering central atoms coordinated to it. For intermediates being formed by a non-dissociative mechanism in complexes with polydentate ligand, different structures were suggested [1, 2, 12]. From the data obtained it is not possible to establish what type of intermediates were formed in our systems. The intermediate undergoes decomposition to the original reactants ($k_2$), or to the thermodynamically more stable $NiN_2S_2R_2$ complex ($k_3$). Under the steady-state condition

$$\frac{d[\{Zn(N_2S_2R_2)Ni\}^{2+}]}{dt} = 0, \qquad (6)$$

the equation (4) can be derived from (5). Values of the rate constants of the reaction steps $k_1$, $k_2$ and $k_3$ could not be computed on the basis of the experimental data.

From the rate constant values (Table III) it follows that the factor considerably influencing the rate of reactions (1) is the electron density distribution in complexes, especially on the donor atoms of sulphur and nitrogen. The electrochemical study of Cu(II) complexes with the ligands used led to the conclusion [8] that the highest occupied orbital of $CuN_2S_2(CH_3)_2$ complex was that localized on the central atom (this was also the result of photoelectron spectroscopy measurement [4] and of molecular orbital calculations [5]); for the complexes with other ligands it was that orbital localized on the ligand, namely on the donor atoms. Given the small difference between the orbital energies of 3d-electrons of Cu and Zn atoms ($\Delta E < 1$ eV [13]) it may be assumed that the knowledge gained in studying the electronic structure of Cu(II) complexes will qualitatively hold also for Zn(II) complexes; that means that the electronic structure of $ZnN_2S_2(CH_3)_2$ should be different (localization of HOMO) from the electronic structure of the complexes with other ligands.

Except for the complex with $R = CH_3$, it has been found that the dependence of log k on the values of Taft's parameters σ of the substituents R [14] (Table III) is linear; the proportionality constant $\rho = -0.538$ is obtained, thus confirming the electrophilic character of the investigated reactions.

The obtained results allow us to conclude that for the reactions investigated in the present work the rate determining step will involve the coordination of $Ni^{2+}$ ion to the $ZnN_2S_2R_2$ complex, since the complex affinity for this step increases with the increasing negative charge localized on the donor ligand atoms.

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