

Ligand Exchange Reactions Between Copper(II)- and Nickel(II)-Chelates of Different Sulfur- and Selenium-Containing Ligands. VI [1]. Kinetics of Ligand Exchange Reactions Studied by Stopped-Flow ESR

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Abstract

The kinetics of ligand exchange reactions studied by means of stopped-flow ESR measurements are reported. The concentration-time curves recorded for all reactions investigated correspond to simple second-order rate laws. The rate constants of the reactions between copper(II) dithiolenes and $\text{Cu}(\text{Et}_2\text{dsc})_2$ (Et_2dsc = diethyldiselenocarbamate) or $\text{Ni}(\text{Et}_2\text{dsc})_2$ were found to be: $[\text{Cu}(\text{mnt})_2]^{2-}$ (mnt = maleonitriledithiolate) + $\text{Cu}(\text{Et}_2\text{dsc})_2$, $k_2 = (2.3 \pm 0.3) \cdot 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$; $[\text{Cu}(\text{mnt})_2]^{2-}$ + $\text{Ni}(\text{Et}_2\text{dsc})_2$, $k_2 = (2.1 \pm 0.1) \cdot 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ and $[\text{Cu}(\text{dmit})_2]^{2-}$ (dmit = isotrithione-3,4-dithiolate) + $\text{Ni}(\text{Et}_2\text{dsc})_2$, $k_2 = (2.5 \pm 0.3) \cdot 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$. A rate constant of $k_2 = (2.0 \pm 0.3) \cdot 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ was determined for the reaction between $\text{Cu}(\text{Et}_2\text{dsc})_2$ and $\text{Cu}(\text{Et}_2\text{dtc})_2$ (Et_2dtc = diethyldithiocarbamate).

Additional experiments suggest a chain mechanism for the ligand exchange reactions in which the monochelates *e.g.* $[\text{Cu}(\text{mnt})]_s$ react as active sites.

Introduction

ESR spectroscopy has been widely used to study ligand exchange reactions in which Cu(II) complexes with unsaturated sulfur- and selenium-containing ligands participate [2–7]. The large number of reactions investigated led to a classification of ligand exchange reactions outlined in [2]:

(I) Reactions between five-membered-ring chelates (dithiolene ligands) and four-membered-ring chelates (ligands: dichalcogeno-carbamate, -xanthogenate, -phosphate and 1,1-substituted-2,2-dichalcogenolates) yield the mixed-ligand complex exclusively.

(II) The exchange reactions between similar four-membered-ring chelates (ligands: dichalcogeno-carbamates and 1,1-disubstituted ethylene-2,2-dichalcog-

enolates) were found to have an equilibrium constant of $K = 4$.

(III) Reactions between complexes containing strongly different ligands could not be classified as unitary.

This classification is also true if the reactions take place between corresponding Ni(II) and Pd(II) chelates.

In contrast to ligand substitution or metal exchange reactions [8–24], few investigations are known concerning the kinetics of the reactions under discussion [25–28]. Kinetic studies on ligand exchange reactions are difficult in most cases because (i) many reactions are fast, and flow or rapid mixing techniques are necessary for observing the reaction rate, and (ii) spectroscopic methods are restricted to those systems in which the ternary complex gives rise to characteristic absorptions. The advantage of ESR spectroscopy is that in ligand exchange reactions between paramagnetic transition metal complexes with different sulfur or selenium donor atom sets, and approximately the same symmetry, all species can be observed in the spectra. However, the conventional ESR allows kinetic measurements only for very slow reactions, as was shown for the system $[\text{Cu}(\text{mnt})_2]^{2-}$ (mnt = maleonitriledithiolate) and $[\text{Pd}(\text{i-mns})_2]^{2-}$ (i-mns = iso-maleonitrilediselenolate, $(\text{CN})_2\text{C} = \text{CSe}_2^{2-}$) [25]. The adaption of a stopped-flow equipment to an ESR spectrometer increases the time resolution by orders of magnitude. By means of this technique we investigated the reactions of $[\text{Cu}(\text{mnt})_2]^{2-}$ with $\text{Cu}(\text{Et}_2\text{dsc})_2$ (Et_2dsc = diethyldiselenocarbamate), $[\text{Cu}(\text{mnt})_2]^{2-}$ with $\text{Ni}(\text{Et}_2\text{dsc})_2$, $[\text{Cu}(\text{dmit})_2]^{2-}$ (dmit = iso-trithione-3,4-dithiolate) with $\text{Ni}(\text{Et}_2\text{dsc})_2$, which belong to type I of ligand exchange reactions, and of $\text{Cu}(\text{Et}_2\text{dsc})_2$ with $\text{Cu}(\text{Et}_2\text{dtc})_2$, corresponding to type II of the above mentioned classification.

Experimental

The stopped-flow equipment was manufactured by the Center of Scientific Instruments of the Academy of Sciences of the G.D.R. In the system used the liquid reactants are stored in two syringes. The plunger of the syringes are pulse-shaped driven by electromagnets. Therefore, high power acceleration of liquids and economical consumption of substances (80 μl per shot) is available. Each syringe contains 1.5 ml reactant, giving 16 shots for spectral accumulation without refilling. The mixer is located near the entrance of the ESR active volume. The ESR sample cell is a cylindrical quartz tube with 1.3 mm internal diameter and 3 mm thickness of wall, being suitable also for aqueous solutions and adaptable to the H_{102} rectangular X-band cavity. Flexible teflon hoses between the syringes and the sample cell, as well as a suitable holding of the mixer-cell, avoid disturbing microphonics. All materials in contact with the reactants are inert against acidic, alkaline or organic solvents. The time resolution of the stopped-flow ESR apparatus is 1 ms and the mixing efficiency is better than 95%. All other details of the stopped-flow equipment are described in [29].

All measurements were performed at 295 K using an E 3 (Varian) spectrometer.

The ionic complexes needed for the measurements were dissolved in acetone and the neutral ones in chloroform. Hence, for the reactions of type I the resulting solvent was a 1:1 mixture of acetone and chloroform. The concentrations of complex solutions were $5 \times 10^{-4} \text{ mol l}^{-1}$, $2,5 \times 10^{-4} \text{ mol l}^{-1}$ and $1 \times 10^{-4} \text{ mol l}^{-1}$.

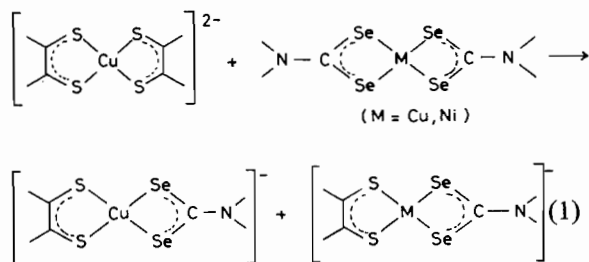
The use of equimolar solutions prevents metal exchange reactions.

The complexes used for the kinetic measurements were prepared according to standard literature methods: $(n\text{-Bu}_4\text{N})_2[\text{Cu}(\text{mnt})_2]$ [30], $(n\text{-Bu}_4\text{N})_2[\text{Cu}(\text{dmit})_2]$ [31], $\text{Cu}(\text{Et}_2\text{dte})_2$ [32], $\text{Cu}(\text{Et}_2\text{dsc})_2$ and $\text{Ni}(\text{Et}_2\text{dsc})_2$ [33].

Results

Reactions of Cu(II) Dithiolenes with $\text{Cu}(\text{Et}_2\text{dsc})_2$ or $\text{Ni}(\text{Et}_2\text{dsc})_2$

The reaction of Cu(II) dithiolenes with Cu(II) or Ni(II) diselenocarbamate complexes belongs to the above mentioned type I of exchange reactions, where the mixed-ligand complex is formed exclusively (1). Therefore, during the reaction of e.g. $[\text{Cu}(\text{mnt})_2]^{2-}$ and $\text{Cu}(\text{Et}_2\text{dsc})_2$ the signals of the parent complexes vanish and the intensity of the peaks corresponding to the mixed-ligand complex increases until the reaction is finished. If the diamagnetic $\text{Ni}(\text{Et}_2\text{dsc})_2$ participates in the reaction the spectra of the Cu(II) dithiolene complex and the ternary complex can be



observed. Figure 1 shows the ESR spectrum of the reaction mixture at $t = 0$ and after completion of the reaction. The field positions used for recording the concentration-time curves are indicated by arrows. The time curve of the reaction and the plot of $1/[A]$ ($A = [\text{Cu}(\text{mnt})_2]^{2-}$) versus t corresponding to a second-order rate law are given in Fig. 2. The following second-order rate constants could be obtained by graphical analysis of the kinetic curves:

$$\text{Cu}(\text{mnt})_2^{2-} + \text{Cu}(\text{Et}_2\text{dsc})_2, k_2 = (2.3 \pm 0.3) \cdot 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$$

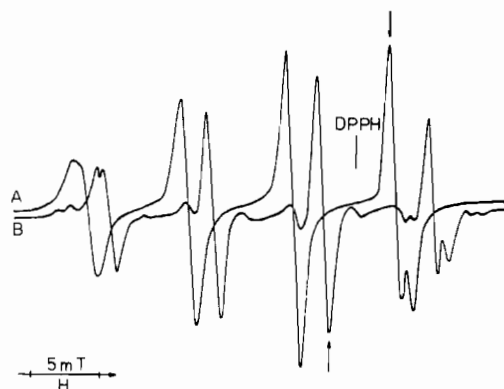


Fig. 1. X-band ESR spectrum of $[\text{Cu}(\text{mnt})_2]^{2-}$ (A) and $[\text{Cu}(\text{mnt})(\text{Et}_2\text{dsc})]^{-}$ (B) recorded at 298 K. The observer peaks for the concentration-time curves are marked by arrows.

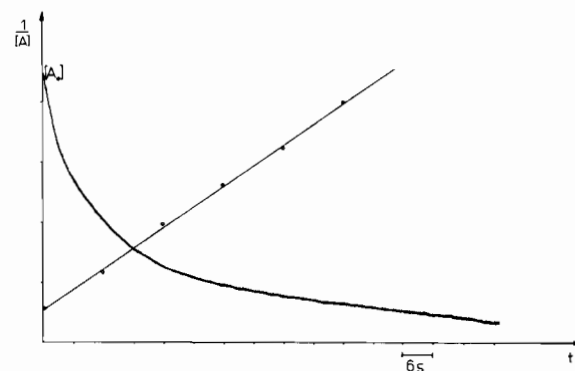
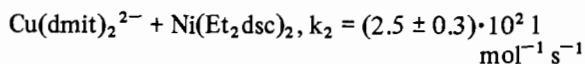
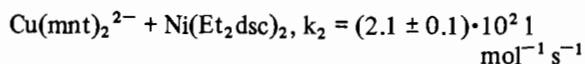


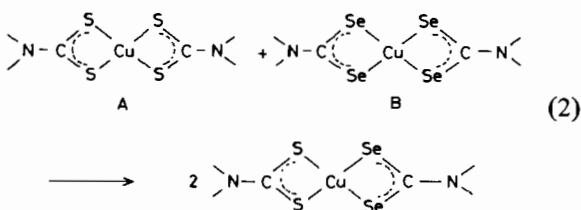
Fig. 2. Concentration-time curve for the decay of $[\text{Cu}(\text{mnt})_2]^{2-}$ in the reaction with $\text{Ni}(\text{Et}_2\text{dsc})_2$ and representation of $1/[A]$ versus t .



In order to get more information about the mechanism of the ligand exchange the reaction of $[\text{Cu}(\text{mnt})_2]^{2-}$ with $\text{Ni}(\text{Et}_2\text{dsc})_2$ was studied by adding Na_2mnt or $(n\text{-Bu}_4\text{N})_2[\text{CuBr}_4]$. Small amounts of free ligands retard the reaction whereas $\text{Cu}(\text{II})$ ions increase the reaction rate. For high ligand concentrations (ratio: $[\text{Cu}(\text{mnt})_2]^{2-} : \text{Ni}(\text{Et}_2\text{dsc})_2 : \text{mnt}^{2-} = 1:1:1$) the reaction follows first-order kinetics with $k_1 = (2.7 \pm 0.5) \cdot 10^{-4} \text{ s}^{-1}$. A rate constant $k_2 = (9.8 \pm 0.4) \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ was evaluated for the reaction catalysed by $\text{Cu}(\text{II})$ ions (ratio: $[\text{Cu}(\text{mnt})_2]^{2-} : \text{Ni}(\text{Et}_2\text{dsc})_2 : [\text{CuBr}_4]^{2-} = 1.5:1.5:1$).

Reaction of $\text{Cu}(\text{Et}_2\text{dtc})_2$ with $\text{Cu}(\text{Et}_2\text{dsc})_2$

In reaction (2) exactly half of the initial binary complexes is transformed into the mixed-ligand complex, the equilibrium constant is equal to $K = 4$. The ESR spectra of the parent complexes and the



spectrum for the equilibrium state are given in Fig. 3. The concentration-time dependencies observed can be reproduced if a rate law corresponding to a reversible bimolecular reaction is used (3):

$$\frac{d[A]}{dt} = k_{-2}[AB]^2 - k_2[A][B] \quad (3)$$

When the initial concentrations of A and B are the same and $K = 4$ the following equation is obtained by integration (x denotes the concentration of A (or B)):

$$-\ln\left(1 - \frac{2x}{[A_0]}\right) = k[A_0]t \quad (4)$$

The recorded concentration-time curve is given in Fig. 4. From the graphical representation of eqn. 4 the rate constant was evaluated as $k_2 = (2.0 \pm 0.3) \cdot 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$. By means of the common relation $K = k_2/k_{-2}$ k_{-2} was found to be equal to $(5.0 \pm 0.3) \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$.

Discussion

Simple second-order rate laws could be evaluated for all reactions investigated. However, as indicated by the exchange reactions which were studied in

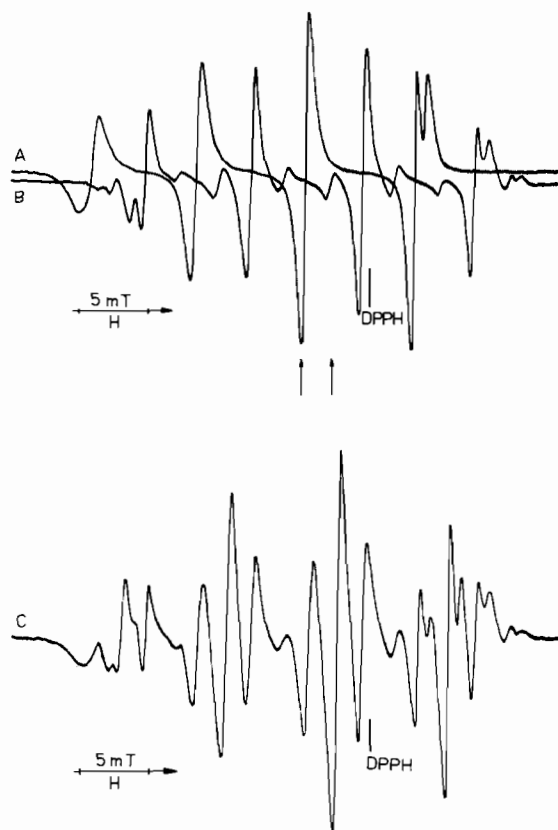


Fig. 3. X-band ESR spectra of the parent chelates $\text{Cu}(\text{Et}_2\text{dtc})_2$ (A), $\text{Cu}(\text{Et}_2\text{dsc})_2$ (B) and the equilibrium mixture of the exchange reaction (C) recorded at 298 K.

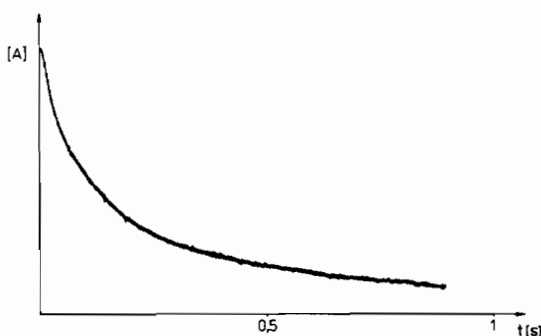


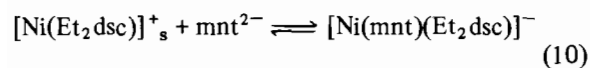
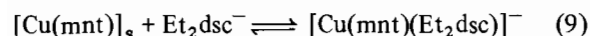
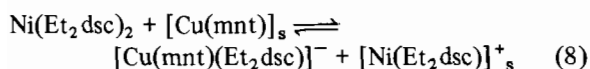
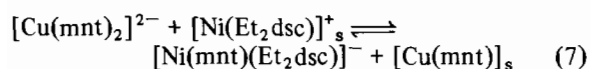
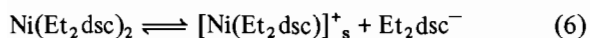
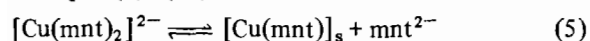
Fig. 4. Concentration-time curve for the reaction of $\text{Cu}(\text{Et}_2\text{dtc})_2$ with $\text{Cu}(\text{Et}_2\text{dsc})_2$. Observer peak: $m_1 = +1/2$ of $\text{Cu}(\text{Et}_2\text{dtc})_2$.

presence of free mnt^{2-} ligands or $\text{Cu}(\text{II})$ ions the reaction mechanism is more complicated and the rate laws should be mainly caused by the rate determining step.

For the reaction between $[\text{Cu}(\text{mnt})_2]^{2-}$ and $[\text{Pd}(\text{i-mns})_2]^{2-}$ [25] a similar behaviour was observed: the addition of mnt^{2-} or i-mns^{2-} ligands inhibits the reaction whereas $\text{Cu}(\text{II})$ ions catalyse the ligand exchange. Because this reaction could be studied by means of the conventional ESR technique the tem-

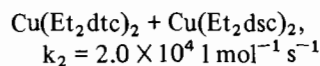
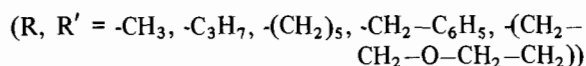
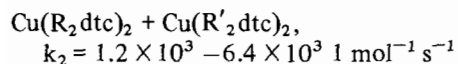
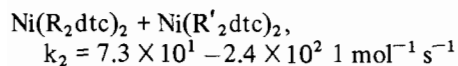
perature dependence of the reaction rate was recorded. The concentration-time curves correspond to a second-order rate law at higher temperatures only (333 K). At lower temperatures the kinetic curves recorded for the reaction product $[\text{Cu}(\text{mnt})(\text{i-mns})]^{2-}$ are indicative for a complex reaction mechanism. Furthermore, the solvent dependence of the reaction rate was investigated. The rate depends strongly on the donor strength of the solvents used.

In accordance with these experimental results the first reaction step should be the dissociation of the parent chelates as shown by reactions (5) and (6) for $[\text{Cu}(\text{mnt})_2]^{2-}$ and $\text{Ni}(\text{Et}_2\text{dsc})_2$, respectively. The solvated 1:1-chelates formed in eqns. (5) and (6) react as the active sites of a chain reaction with the corresponding binary complexes to yield the mixed-ligand chelates. The hole chain mechanism is given by the eqns. (5)–(10):



Several attempts have been made to afford a proof for the existence of the 1:1-chelates proposed as essential members in the chain mechanism. The halogenide stabilized species involving one mnt^{2-} or $\text{R}_2\text{-dsc}^-$ ligand only could be characterized by ESR spectroscopy [34] and the reaction of $\text{M}(\text{R}_2\text{dsc})_2$ complexes with corresponding metal ions (e.g. Cu(II), Ni(II), Zn(II)) yield likewise the mono-chelates indicated by their electronic spectra [35]. These results confirm the dissociative start mechanism although there is no spectral evidence for the solvated 1:1-chelates during the exchange reaction.

Finally some remarks should be made concerning the exchange reaction between $\text{Cu}(\text{Et}_2\text{dsc})_2$ and $\text{Cu}(\text{Et}_2\text{dsc})_2$. The rate law obtained for this reaction is similar to that of the ligand exchange of Ni(II) or Cu(II) dithiocarbamates containing different substituents R evaluated by means of HPLC [27]. The rate constants determined are in the expected order of magnitude:



No further experiments are published to give information about the mechanism of this reaction type. However, the observation of the mono-chelates $[\text{M}(\text{R}_2\text{dsc})]_s^+$ suggest that the mechanism should be similar to that proposed in eqns. (5)–(10).

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