Kinetic Studies of Fast Equilibrium by Means of High-performance Liquid Chromatography. II. Ligand Exchange of *N,N*-Disubstituted Dithiocarbamate Chelates of Ni(II)

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The equilibrium of the ligand exchange of labile Ni(II) dialkyldithiocarbamate chelates ($MA_2+B \rightleftarrows MAB+A$, $MAB+B \rightleftarrows MB_2+A$, $K_1=[MAB][A]/[MA_2][B]$, $K_2=[MB_2][A]/[MAB][B]$) has been investigated by means of high-perfromance liquid chromatography, two solutions of MA_2 and B being mixed and then equilibrated. The equilibrium constants, K_1 and K_2, have been determined by measuring the concentrations of each complex, including the kinetically unstable ternary complex in the equilibrium state. The ratio of the stability constants of the two Ni(II) chelates, which is equal to K_1K_2, has been calculated. The following series of increasing stability constants has been found for the alkyl substituents in chloroform; tetramethylene<dimethyl<pentamethylene<diethyl<hexamethylene<dipropyl<dibutyl. The rate of ligand exchange has been investigated by mixing very dilute MA_2 and B and by injecting the mixture into HPLC after the lapse of a certain time. The rate of ligand exchange is slow when low initial concentrations of MA_2 and B are chosen. The rate of ligand exchange is more than ten times faster than that of ternary complex formation.

In our previous studies[1,2] the equilibrium of the labile ternary-complex formation of *N,N*-disubstituted dithiocarbamate chelates of Ni(II) and Cu(II) was investigated by means of high-performance liquid chromatography (HPLC). The labile ternary complex, which is formed by mixing two solutions of the corresponding binary complexes, undergoes disproportionation as soon as it is separated from binary complexes in the column. The separation process of HPLC is so rapid that it might compete with the progress of disproportionation during the course of chromatography. In HPLC there are some factors serving to retard disproportionation in the column: (1) Each species is diluted rapidly in the column, suppressing the disproportionation which can be anticipated to occur by means of the bimolecular collisional process of two binary complexes. (2) The rate of disproprotionation can be controlled by a suitable choice of initial concentrations of two binary complexes, disproprotionation being slow when the initial concentrations are low. (3) The control of the column temperature will be effective, disproportionation being retarded when the column temperature is kept low. By the combination of these factors, disproportionation during chromatography is retarded effectively, and chromatograms obtained directly indicate the concentrations of each species before chromatography. Thus, it becomes possible to trace quite fast bimolecular reactions by means of HPLC. In our previou studies, the equilibrium constants and rate constants of labile ternary complex formation of *N,N*-disubstituted dithiocarbamate chelates of Ni(II) and Cu(II) were determined in this way. The present article shows that HPLC can also be applied to the kinetic investigation of ligand exchange in solution. We have chosen Ni(II) chelates because the rate of the ligand exchange of Ni(II) chelates is moderately fast and so the determination of the kinetic characteristics can be carried out by means of HPLC.

Experimental

Reagents. Sodium salts of *N,N*-disubstituted dithiocarbamates were prepared and purified as has been reported previously.[2] Diethylammonium salt of diethyldithiocarbamic acid was purchased commercially (Nakarai Chemicals, Ltd.). Dipropylammonium salt of dipropyldithiocarbamic acid was prepared as follows. In a 500-cm^3 of flask, 0.2 mol of dipropylamine dissolved in 100 cm^3 of hexane was placed. The flask was cooled in an ice bath, and then 0.1 mol of carbon disulfide in 100 cm^3 of hexane was stirred in, drop by drop. A voluminous white product was gradually precipitated. After having been washed with hexane, the product was dried in a vacuum desiccator. This product was found to be >98% pure when the content was determined to be Ni(II) chelates by colorimetry. It was used without further purification, because recrystallization from water gave worse results as a result of the formation of disulfide compounds (mainly *N,N,N',N'*-tetrapropylthiuram disulfide) on heating.

The concentration of the Ni(II) standard solution (0.01 mol dm^{-3} $NiCl_2$) was determined to be Ni(II) diethyldithiocarbamate by colorimetry. All the solvent used for the eluent were saturated with water before use, as had been reported previously.[2]

Apparatus. The apparatus used in this study was identical with that used in our previous reports.[1-3]

Procedure. The metal chelates were prepared by mixing the Ni(II) standard solution and the sodium salts of the corresponding dialkyldithiocarbamic acids. The metal chelates produced were extracted with chloroform under the condition of a complete extraction (pH 4.0 acetate buffer). The chloroform layer was washed with a 1% sodium hydrocarbonate solution four times to remove the residual free ligands in chloroform. Thus, solutions of each metal chelate (0.5 to 1.0×10^{-3} mol dm^{-3}) were prepared. These solutions were stable for at least three weaks when stored in a refrigerator. Solutions of dialkylammonium salts of dialkyldithiocarbamic acids were prepared by dissolving the corresponding salts in chloroform. These solutions were newly prepared before use, for they were not very stable and disulfide-degradation compounds were gradually produced on storage. The contents of these solutions were determined after the formation of Ni(II) chelates as will be shown in the following section.

For the determination of the equilibrium constants and rate constants, each solution was thermostated at 25 °C. All the measurements were carried out at least three times.

Theoretical

HPLC Analysis of Equilibrium of Ternary-complex Formation. The HPLC method for the analysis of a fast equilibrium in solution is, in principle, a conventional one. When two labile binary complexes, MA_2 and MB_2, are mixed in the absence of excess free ligands, the following ternary-complex formation will be equilibrated promptly.

$$MA_2 + MB_2 \underset{k_-}{\overset{k}{\rightleftharpoons}} 2MAB, \quad (1)$$

$$K = [MAB]^2/[MA_2][MB_2]. \quad (2)$$

When the separation speed of HPLC is so fast that the disproportionation of the kinetically unstable ternary complex MAB is negligible during the course of chromatography, K can be determined by measuring the peak heights of each chelate that appears on the chromatograms.

The rate constants, k and k_-, will be determined as follows assuming a simple bimolecular rate equation. When two dilute solutions of MA_2 and MB_2 are mixed, a ternary complex, MAB, is gradually produced according to the following equation:

$$\frac{d[MAB]}{dt} = k[MA_2][MB_2] - k_-[MAB]^2. \quad (3)$$

Taking the initial concentrations of MA_2 and MB_2 to be a_0 and b_0 respectively, we obtain:

$$\frac{dx}{dt} = k(a_0-x/2)(b_0-x/2)-k_-x^2$$
$$= -(kx^2/4)(4/K-1) - (kx/2)(a_0+b_0)+a_0b_0k, \quad (4)$$

where x is the concentration of MAB. We obtain the following equations by integrating Eq. 4:

$$k = -[2/(a_0+b_0)t] \ln [1-(a_0+b_0)x/2a_0b_0], \quad (5)$$
$$(K=4.0)$$

$$k = (2/m_0t)\left[\ln \frac{\left(\frac{a_0+b_0+m_0}{1-K/4}-x\right)}{\left(\frac{a_0+b_0-m_0}{1-K/4}-x\right)} + \ln \left(\frac{a_0+b_0-m_0}{a_0+b_0+m_0}\right)\right], \quad (6)$$
$$(K\neq 4.0)$$

where $m_0=\sqrt{(a_0+b_0)^2-4a_0b_0(1-4/K)}$. Thus, the two rate constants k and k_- can be determined from Eqs. 5 and 6.

HPLC Analysis of the Equilibrium of Ligand Exchange and Determination of the Relative Stability Constants of Metal Chelates. When the free ligand B is added to a solution containing only one kind of binary complex, MA_2, the following ligand exchange will occur in the mixture:

$$MA_2 + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MAB + A, \quad (7)$$

$$MAB + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MB_2 + A, \quad (8)$$

$$K_1 = [MAB][A]/[MA_2][B], \quad (9)$$

$$K_2 = [MB_2][A]/[MAB][B]. \quad (10)$$

From Eqs. 2, 9, and 10, it follows that:

$$K_1/K_2 = [MAB]^2/[MA_2][MB_2] = K. \quad (11)$$

The product of the two equilibrium constants, K_1K_2, is the ratio of the stability constants of the two binary complexes as is shown below:

$$K_1K_2 = [MB_2][A]^2/[MA_2][B]^2 = \beta_{MB_2}/\beta_{MA_2}, \quad (12)$$

$$\beta_{MA_2} = [MA_2]/[M][A]^2, \quad (13)$$

$$\beta_{MB_2} = [MB_2]/[M][B]^2. \quad (14)$$

These equilibrium constants will be determined if the equilibrium concentrations of each species are determined by HPLC. The rate constants of the ligand exchange can also be obtained by observing the change in the chromatogram patterns after mixing two solutions of MA_2 and B. It should be noted here that, being different from equilibrium constants, the two rate constants k_1 and k_2 vary independently of each other. This complicates the determination of these characteristics. When the initial concentration of MA_2 ($=a$) is much larger than that of B($=b$), the formation of MB_2 in the equilibrium state can be neglected. In this case, we can neglect the equilibrium shown in Eq. 8, and the following equation is obtained if the rate of ligand exchange can be expressed by a simple bimolecular-rate equation including $[MA_2]$ and [B]:

$$\frac{dx}{dt} = k_1(a-x)(b-x)-k_{-1}x^2$$
$$= k_1(1-1/K_1)x^2 - (a+b)k_1x + abk_1. \quad (15)$$

Equation 15 can then be integrated to give:

$$k_1 = -[1/(a+b)t]\ln[1-(a+b)x/ab] \quad K_1=1.0, \quad (16)$$

$$k_1 = (1/mt)\left[\ln \frac{\left(\frac{a+b+m}{2(1-1/K_1)}-x\right)}{\left(\frac{a+b-m}{2(1-1/K_1)}-x\right)} + \ln\left(\frac{a+b-m}{a+b+m}\right)\right], \quad (17)$$
$$K_1\neq 1.0$$

where $m=\sqrt{(a+b)^2-4ab(1-1/K_1)}$.

Results and Discussion

Equilibrium Constants of Ligand Exchange and the Relative Stability of Ni(II) Chelates. Some examples of chromatograms for determining the equilibrium constants, K_1 and K_2, are shown in Fig. 1. Here, for A and B we have chosen $(CH_2)_6NCSS^-$ and $(C_3H_7)_2NCSS^-$ respectively. Standard solutions of MA_2 and MB_2 were diluted with chloroform to various concentrations, and 5-μl portions of these solutions were injected into the column (Figs. 1(a) and (b)). Linear calibration graphs were obtained for MA_2 and MB_2 within a wide range of sample amounts. Then solutions of MA_2 and MB_2 were mixed so that the initial concentrations were equivalent ($=a_0$). In the mixture, the ternary-complex MAB was gradually formed, and after it had stood for some time, equilibrium was attained. The equilibrium concentrations of MA_2, MB_2, and MAB are $a_0/2$, $a_0/2$, and a_0 respectively, because the ternary-complex formation in this case is known to be controlled by a statistical factor ($K=4.0$).[1,2] Then the equilibrated solution was diluted to various concentrations, and these portions were injected into the column (Fig. 1(c)). Calibration graphs of MAB, which were also linear, were obtained in this way.

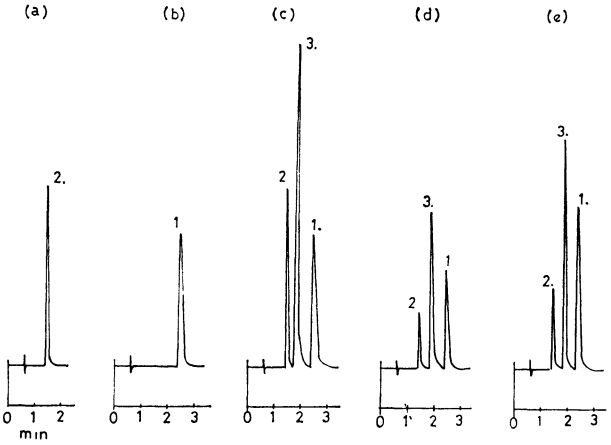

Fig. 1. Chromatogram patterns of the mixture of Ni[$(CH_2)_6NCSS]_2$ and $(C_3H_7)_2NCSS^-$.
Column: Shodex silipak (4 mm × 15 cm). Eluent: hexane: ethyl acetate = 100 : 8 (water saturated). Flow rate: 2.5 cm^3/min. Detector: 325 nm. Sample size: 5 μl. Sample: (a) 0.25 mmol dm^{-3} $Ni[(C_3H_7)_2NCSS]_2$ (=NiB_2) in chloroform; (b) 0.25 mmol dm^{-3} $Ni[(CH_2)_6NCSS]_2$ (=NiA_2) in chloroform; (c) 0.50 mmol dm^{-3} NiA_2 + 0.50 mmol dm^{-3} NiB_2 in chloroform. Equilibrium concentrations of NiA_2, NiB_2, and NiAB were 0.25, 0.25, and 0.50 mmol dm^{-3}, respectively;[2] (d) 0.50 mmol dm^{-3} NiA_2 + b (=0.58_0) mmol dm^{-3} B in chloroform. Equibrium concentrations of NiA_2, NiB_2, and NiAB were determined to be 0.18_5, 0.07_{73}, and 0.24_4 mmol dm^{-3}, respectively. Total concentration of Ni(II) was calculated to be 0.50_5 mmol dm^{-3}. (a=0.50 mmol dm^{-3}); (e) Solution of (d) and aqueous $NiCl_2$ solution were mixed, and the mixture was shaken vigorously for about 20 s. After standing for some time the chloroform layer was supplied to HPLC. Equilibrium concentrations of NiA_2, NiB_2, and NiAB were 0.31_0 0.11_1, and 0.35_8 mmol dm^3, respectively. Thus concentration of b was calculated to be $0.11_1 \times 2 + 0.35_8 = 0.58_0$ mmol dm^{-3}. Total concentration of A was $0.31_0 \times 2 + 0.35_8 = 0.97_8$ ($2a$=1.00 mmol dm^{-3}).
1: NiA_2, 2: NiB_2, 3: NiAB.

Two solutions of MA_2 and B, whose initial concentrations were a and b, were then mixed at 25 °C. When a and b were relatively large (about 1×10^{-3} mol dm^{-3}), the equilibrium of ligand exchange occurred almost instantaneously after mixing. The equilibrated solution was divided into two parts, and a 5-μl portion of one part (Soln A) was supplied to HPLC (Fig. 1(d). Peaks corresponding to MA_2, MB_2 and MAB appeared on the chromatograms. Since free dithiocarbamates have no absorption at 325 nm, peaks of the free ligands, A and B, did not appear on the chromatograms. Injection into the column should be carried out within 10 min after mixing, otherwise, some errors were observed due to the gradual decomposition of the free ligands (probably attributable to the formation of disulfide compounds). The total concentration of Ni(II) of MA_2, MB_2, and MAB in the equilibrium state was equal to the initial concentration of MA_2(=a), within the limit of experimental error as is shown in Fig. 1. Thus, the concentrations of MA_2, MB_2, and MAB in the equilibrium state were determined. The concentration of the free ligand A was calculated by means of this equation: $[A] = 2a - 2[MA_2] - [MAB]$. The concentration of the free ligand B was determined as follows: to the residual part of the equilibrated solution mentioned above, an aqueous nickel chloride solution was added, after with the mixture was shaken vigorously for about 20 s. Thus, free ligand residing in chloroform reacted with Ni(II) to form metal chelates, which were then extracted into chloroform quantitatively. Then the solution (Soln B) was supplied to HPLC (Fig. 1(e)). The total concentration of B was thus determined, and the concentration of [B] in Eqs. 9 and 10 was calculated. Here, the total concentration of the A ligand in Soln B should be equal to $2a$: this was confirmed as is shown in Fig. 1(e). Now, since the concentrations of $[MA_2]$, $[MB_2]$, [MAB], [A], and [B] in Eqs. 9 and 10 were determined, K_1 and K_2, and, therefore, K and K' could be calculated.

With similar procedures, the K_1 and K_2 for the system composed of other Ni(II) dialkyldithiocarbamates and dipropylammonium salt of dipropyldithiocarbamic acid were determined. The results are summarized in Table 1. The K_1/K_2 ratio, which are equal to the equilibrium constants of ternary-complex formation, were always

Table 1. Equilibrium constants of ligand exchange and relative stability constants of Ni(II) dithiocarbamate chelates

$NiA_2 + B \rightleftharpoons NiAB + A$, $K_1 = [NiAB][A]/[NiA_2][B]$
$NiAB + B \rightleftharpoons NiB_2 + A$, $K_2 = [NiB_2][A]/[NiAB][B]$
$NiA_2 + NiB_2 \rightleftharpoons 2NiAB$, $K = [NiAB]^2/[NiA_2][NiB_2]$.

A	K_1	K_2	$K_1K_2 = \beta_{MB_2}/\beta_{MA_2}$	$K_1/K_2 = K$	Retention time/min			Eluent
					MA_2	MAB	MB_2	
$(CH_3)_2NCSS^-$	6.1 ±0.15	1.8 ±0.2	11.1 ±2.1	3.4±0.7	3.4	1.8	1.1	A
$(C_2H_5)_2NCSS^-$	3.3 ±0.2	0.77±0.04	2.5 ±0.3	4.3±0.5	2.4	1.8	1.4	B
$(C_4H)_2NCSS^-$	1.43±0.13	0.32±0.03	0.46±0.09	4.5±0.8	1.4	1.7	2.2	C
$(CH_2)_4NCSS^-$	12.7±1.2	3.4 ±0.3	43.7 ±8.0	3.7±0.8	2.5	1.6	1.1	A
$(CH_2)_5NCSS^-$	4.6±0.4	1.1 ±0.1	5.1 ±0.9	4.1±0.4	3.3	2.1	1.4	B
$(CH_2)_6NCSS^-$	2.8±0.2	0.67±0.05	1.8 ±0.25	4.1±0.5	2.4	1.8	1.4	B

B: $(C_3H_7)_2NCSS^-$, in chloroform, 25 °C, Chromatographic conditions: column: Shodex silipak (4 mm × 15 cm), eluent: hexane: ethyl acetate (water saturated) = 100 : 15(A), 100 : 8 (B), 100 : 3.5(C), flow rate: 2.5 cm^3/min, detector: 325 nm, sample size: 5 μl.

equal to 4 within the limit of experimental error, as was predicted by the results of our previous reports.[1,2] The ratios of the stability constants ($\beta_{MB_2}/\beta_{MA_2}=K_1K_2$) shown in Table 1 suggest that the following order of increasing stability constants was found for alkyl substituents: tetramethylene<dimethyl<pentamethylene<diethyl<hexamethylene<dipropyl<dibutyl. It is well known that the introduction of an alkyl group into chelate reagents has a tendency to stabilize the chelates formed, because the alkyl group shows electron-donating effect, and therefore, the acidity of the chelate reagents is decreased. It seems that the present results can be well interpreted in terms of such electron-donating effects of the alkyl group. The stability constants of dithiocarbamate chelates, including Ni(II) chelates, were investigated by Scharfe *et al.*,[4] and the following order of increasing stability constants was indicated for Ni(II) chelates: diethyl<tetramethylene<pentamethylene<hexamethylene. The discrepancy between their results and the present one with respect to the relationship between cyclic and acyclic alkyl substituents might be interpreted in terms of the difference in the solvent. Janssen[5] scrutinized the stability constants of Cu(II) dialkyldithiocarbamate chelates in a mixed solution of water : ethanol by the spectroscopic method. His results on the order of stability constants as to alkyl substituents were identical with those of our present work.

Rate of Ligand Exchange. There remains some difficulties in the determination of the rate constants of ligand exchange. (1) When the concentrations of MA_2 and B were relatively large, ligand exchange was equilibrated instantaneously after mixing. In order to decrease the rate of ligand exchange enough for determination by HPLC, the initial concentrations of MA_2 and B should be chosen so as to be of the order 10^{-6} mol dm^{-3}, close to the detection limit of the UV detector. (2) If the concentrations of MA_2 and B were chosen to be close to each other, the two steps of ligand exchange shown in Eqs. 7 and 8 should occur simultaneously. This will complicate the determination of the rate constants because k_1 and k_2 vary independently. Therefore, the two solutions of MA_2 and B should be mixed so that only the first step of ligand exchange occurs predominantly ($[MA_2]\gg[B]$). Too much excess of MA_2, however, is not favorable because the rate of ligand exchange increases with the increase of $[MA_2]$. Thus, the concentration range of a and b suitable for kinetic study is narrow, and a large error is inevitable.

For the determination of the rate constants of ligand exchange, two dilute solutions of $Ni[(C_2H_5)_2NCSS]_2$ ($=MA_2$) and $(C_3H_7)_2NCSSC_3H_7NH$ ($=B$), were mixed at 25 °C. The mixed solution was left to stand for 15 s, 35 s, 2 min, and 5 min, and then a portion of the mixture was submitted to HPLC. Figure 2 illustrates the change in the chromatograms. Measurements for each were made four times. With the lapse of time, the peak of MAB rose, while that of MA_2 fell. Since the initial concentration of MA_2 was chosen to be considerably larger than that of B, the peak of MB_2 did not appear on the chromatograms, the second step of ligand exchange shown in Eq. 8 being negligible.

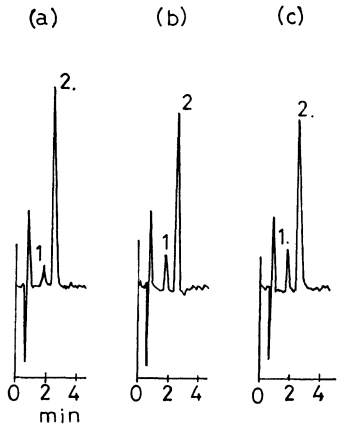

Fig.. 2 Change of chromatogram patterns by ligand exchange. Column: Shodex silipak (4 mm × 15 cm). Eluent: hexane : ethyl acetate = 100 : 8 (water saturated). Flow rate: 2.5 cm^3/min. Detector: 325 nm. Sample size: 200 μl (in chloroform: ethyl acetate: hexane = 1 : 1 : 8). Sample: 5.0×10^{-6} mol dm^{-3} $Ni[(C_2H_5)_2NCSS]_2$ ($=MA_2$) + 7.9×10^{-7} mmol dm^{-3} $(C_3H_7)_2NCSS^-$ ($=B$). (a) After mixing 15 s, (b) 35 s, (c) 3 min (equilibrium).
1 : NiAB, 2 : NiA_2.

The equilibrium was attained within 2 min, as shown by the fact that the chromatograms of the solutions after mixing for 2 and 5 min were identical. The time required to attain equilibrium was approximately inversely proportional to the product of the initial concentrations of MA_2 and B. From these results, the rate constants k_1 and k_{-1} in Eq. 7 can be calculated in terms of Eq. 17 if ligand exchange occurs by means of a bimolecular process. The simple bimolecular mechanism in ligand exchange does not seem to be conclusively proved, however, because of the relatively large experimental error and also because of the following reason. The kinetic study of the ligand exchange of square-planer Pt(II) complexes has been investigated by many workers, and it has been established that the ligand exchange of monodentate ligand proceeds by means of a two-path mechanism, including a five-coordinate intermediate[6] in an aqueous solution. In such cases, the rate of ligand exchange, R, is expressed by the following two-term rate law: ($MA_3X+Y\rightarrow MA_3Y+X$, $R=k[MA_3X]+k'[MA_3X][Y]$). A similar mechanism has been suggested for Ni(II) complexes.[7] Therefore, it seems probable that the rate of ligand exchange of Ni(II) dithiocarbamates might be expressed by a similar two-term rate law, though the present experiments were carried out in a nonaqueous solvent and the ligands involved were bidentate. It can be safely concluded at present that the bimolecular collisional process is predominant, even though the rate equation of ligand exchange is expressed by a two-term rate law or other more complicated equations.[8] If we assume that the simple bimolecular process is valid, the rate constants, k_1 and k_{-1}, in Fig. 2 can be calculated in terms of Eq. 17, because all the variables, K_1, a, b, and x, are known. Thus, k_1 and k_{-1} were calculated to be $(8.3\pm2.4)\times10^3$ mol dm^{-3} s^{-1} and $(2.4\pm0.7)\times10^3$ mol dm^{-3} s^{-1} respectively. The rate constant of ternary-

complex formation between $Ni[(C_2H_5)_2NCSS]_2$ and $Ni[(C_3H_7)_2NCSS]_2$ is $(2.4\pm0.2)\times10^2$ mol dm^{-3} s^{-1}, as was shown in our previous report.[2] The present results show that the rate of ligand exchange is more than ten times faster than that of ternary-complex formation. Considering that the ligand exchange of Ni(II) chelates is so fast that equilibrium is attained promptly at room temperature,[9] the present results seem reasonable.

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