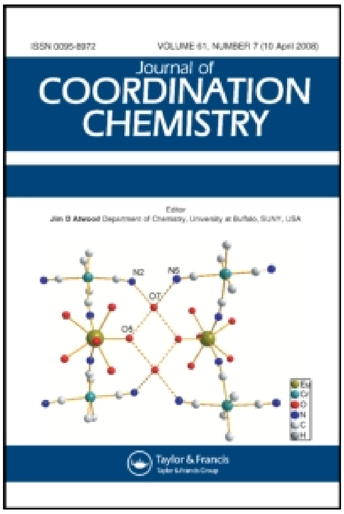

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mudasir, Yoshioka, N. and Inoue, H.(2001) 'LIGAND-EXCHANGE REACTION BETWEEN TRIS(1,10-PHENANTHROLINE)METAL(II) AND TRIS(4,7-DIPHENYL-1,10-PHENANTHROLINE)METAL(II) IONS', Journal of Coordination Chemistry, 52: 4, 333 — 344

To link to this Article: DOI: 10.1080/00958970108028182

URL: http://dx.doi.org/10.1080/00958970108028182

J. Coord. Chem., 2001, Vol. 52, pp. 333–344
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LIGAND-EXCHANGE REACTION BETWEEN TRIS(1,10-PHENANTHROLINE)METAL(II) AND TRIS(4,7-DIPHENYL-1,10-PHENANTHROLINE)METAL(II) IONS

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(Received 4 January 2000; In final form 6 April 2000)

The ligand exchange reaction between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ (where M is the same and $M = Fe^{II}$ or Ni^{II}, phen = 1,10-phenanthroline, DIP = 4,7-diphenyl-1,10-phenanthroline) has been investigated by reversed phase ion-paired chromatography (RP-IPC). The effect of pH and solvent on the ligand-exchange reaction is studied by monitoring the variation in chromatograms with time after mixing. The results have shown that the ligand exchange reaction between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ takes place in the pH range of 3–8 and the rate of reaction for nickel(II) complexes is about two times slower than that for iron(II) complexes. Experiments on the effect of various solvents on the ligand-exchange reaction have revealed that the rate of reaction is enhanced by the solvent in the following order: $(CH_3)_2CO > CHCl_3 \geq CH_2Cl_2 > CH_3CN > CH_3OH$. Elemental analysis and UV-visible spectroscopy confirmed that the products obtained from the ligand-exchange reaction are mixed-ligand complexes containing phen and DIP ligands, *i.e.*, $[M(phen)_2(DIP)]^{2+}$ and $[M(phen)(DIP)_2]^{2+}$.

Keywords: Ligand-exchange reaction; 1,10-phenanthroline; Mixed-ligand complexes; HPLC; Iron(II) and nickel(II)

INTRODUCTION

Despite the excellence of high performance liquid chromatography (HPLC) in the identification, separation and quantitation of many metal complexes

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*Corresponding author. Fax: +81-45-566-1551, e-mail: inoue@applc.keio.ac.jp and organometallic compounds [1], little attention has been attracted to the use of this technique for monitoring inorganic reactions. Some examples of the application of HPLC to such systems [2–4] have demonstrated its large capability and reliability in identification and high-purity isolation of inorganic compounds as well as its usefulness in their kinetic and equilibrium studies. For many years, metal complexes of 1,10-phenanthroline (phen) and its derivatives have been widely applied to the study of the interaction of metal complexes with DNA [5–9]. It is of considerable interest to better understand the behavior of these complexes in solution because their DNA-binding mechanism depends, in part, on the nature of these complexes in solution. 1,10-Phenanthroline and its derivatives are well-known to form relatively stable cationic complexes with a variety of metal ions [10]. We are particularly interested in iron(II) and nickel(II) complexes of phen and its derivatives because their interaction with DNA has not received much attention compared to the corresponding ruthenium(II) complexes. Furthermore, iron(II) and nickel(II) ions are more common in the living body than is ruthenium(II) giving the possibility for *in vivo* study in the future. Iron(II) and nickel(II) complexes of phen are known as labile complexes towards racemization. The racemization of iron(II) complexes takes place in both intra- and intermolecular mechanisms, while that of nickel(II) complexes proceeds only by an intermolecular mechanism [11, 12]. In the intermolecular mechanism of racemization, two molecules of each complex are involved during the process and the exchange of their ligands occurs in solution. Therefore, when two types of iron(II) or nickel(II) complexes of phen and its derivatives are mixed in solution, the ligand-exchange reaction between the two types of complexes is expected to yield mixed-ligand complexes of the corresponding metal ions. Although the aquation, dissociation and racemization of these complexes in various solvents have been extensively studied [13–17], few reports have been published, as far as we know, on the ligand-exchange reaction between two metal complexes of phen and its derivatives. In the present study, we have carried out a detailed study on ligand exchange among metal complexes of 1,10-phenanthroline and its derivatives using the ion-paired reversed-phase HPLC method. To simplify the experimental conditions, only two complexes *i.e.*, $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ have been employed. These two complexes are chromatographically well-separated from each other with large differences in retention time [18] so that the additional peaks are expected to appear between those of the two complexes and can be easily monitored. Here, the effects of pH and various solvents on the ligand-exchange reaction between two complexes have been systematically studied.

EXPERIMENTAL

Materials

1,10-Phenanthroline and 4,7-diphenyl-1,10-phenanthroline were obtained from Dojindo Laboratories (Kumamoto, Japan) and Kanto Chemical Co. Inc. (Tokyo, Japan), respectively and were used for the preparation of metal complexes without further purification. Tris(1,10-phenanthroline)metal(II), $[M(phen)_3]^{2+}$, as their perchlorate salts were prepared by a procedure described by Schilt and Taylor [19]. Tris(4,7-diphenyl-1,10-phenanthroline)metal(II), $[M(DIP)_3]^{2+}$ were synthesized according to our previous report [18]. The salts $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ were purchased from Wako Pure Chemical Industries (Tokyo, Japan). Perchloric acid, $HClO_4$ and $NaClO_4$ were obtained from Junsei Chemical Co. Ltd. (Tokyo, Japan) and Kanto Chemical Co. (Japan), respectively. Acetonitrile (special grade) and distilled water (HPLC grade) for mobile phase were supplied by Katayama Chemical Industries Ltd. The mobile phase was prepared by volume and consisted of acetonitrile-water (80/20, v/v) and 0.06 M $HClO_4$ (or $NaClO_4$) and was ultrasonically mixed for several minutes before use for analysis.

Instrumentation

The absorption spectra were recorded on a Jasco V-550 UV-VIS spectrophotometer (Tokyo, Japan). A model HM-12P pH-meter from TOA Electronics (Japan) was used for pH measurements. The Jasco PU-980 liquid chromatograph (or Jasco BIP-I HPLC pump), equipped with a Reodyne 7125 (100 μl loop) injector, an Inertsil ODS column (5 μm spherical ODS, 250 mm × 4.6 mm I.D., GL Science Co., Tokyo) and a Jasco MULTI-340 multichannel (or a model M-315 variable wavelength) spectrophotometer detector, was used for analytical HPLC. The detector was connected to a Jasco model 807-IT integrator or, in case of a multichannel detector, to a personal computer (NEC PC-980 VM) for the purpose of peak analyses. Semi-preparative HPLC was conducted using a Yanako L-4000 W pump, equipped with a Develosil ODS column (10 μm spherical ODS, 25 cm × 3 cm I.D., Nomura Chemical Co., Aichi, Japan), a Kusano-Kagaku KV-3W loop injector (0.59 mL), and a Jasco Uvidec 100-III UV detector together with a Dip 3066 pen recorder obtained from Yokogawa Electric Work Ltd. (Tokyo, Japan). Elemental analyses were performed by the Central Laboratory, Faculty of Science and Technology, Keio University (Yokohama, Japan).

Procedures

The experiments were carried out as follows; a solution of $[M(phen)_3]^{2+}$ in mobile phase or other solvents, *i.e.*, acetone, chloroform, dichloromethane, acetonitrile and methanol, was mixed in a 25 mL volumetric flask with that of $[M(DIP)_3]^{2+}$ to give a final concentration of 1 μg cm^{-3} for each complex. The molar concentrations of $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ are 1.8×10^{-6} and 9.5×10^{-7} M for iron(II) complexes, and 1.7×10^{-6} M and 9.5×10^{-7} M for nickel(II) complexes. The effect of pH on the ligand exchange reaction was studied by adjusting the pH of the mixing solution and keeping it at room temperature (ca. 20°C). The changes in chromatograms with time after mixing were then monitored by injecting the reaction mixture to the HPLC system and the chromatograms obtained were analyzed.

Determination of Rate Constant

The rate constant (k) in this study is defined as the decreasing rate of reactant concentrations, *i.e.*, the concentration of $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$, due to ligand exchange between the two kinds of complexes. The decrease in concentration of the corresponding complex after mixing is proportional to peak area of the HPLC chromatogram for each complex. By determining the peak area of the complex before the mixing (C_0) and monitoring the decrease in peak area of each complex at various times after the mixing (C_t), we can construct a *pseudo* first-order reaction plot of $\ln(C_t/C_0)$ *vs.* time (t) to yield a linear graph with the slope equal to $-k$.

TABLE I Rate constant (k)[a] and half-life ($t_{1/2}$) of ligand exchange reaction between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ at various pH

pH[b]	$k[h^{-1}]$ $[h]$	$t_{1/2}$ $[h]$	$k[h^{-1}]$	$t_{1/2}$
	$[Fe(phen)_3]^{2+}$		$[Fe(DIP)_3]^{2+}$	
3.0	7.8×10^{-3}	88.9	13.0×10^{-3}	53.3
6.0	8.0×10^{-3}	86.6	12.6×10^{-3}	55.0
8.0	6.5×10^{-3}	106	12.4×10^{-3}	5.9
	$[Ni(phen)_3]^{2+}$		$[Ni(DIP)_3]^{2+}$	
3.0	5.0×10^{-3}	139	6.7×10^{-3}	103
6.0	4.9×10^{-3}	141	6.8×10^{-3}	102
8.0	4.8×10^{-3}	144	7.0×10^{-3}	99.0

[a] Defined as the decreasing rate of reactant concentrations, *i.e.*, the concentration of $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$, due to ligand exchange and is calculated by plotting $ln(C_t/C_0)$ *vs.* t; $t_{1/2} = 0.693/k$; Solvent: CH_3CN-H_2O (80/20, v/v) containing 0.06 M $HClO_4$;

[b] The pH values are expressed as a pH reading of a pH meter and not corrected to the solution in the nonaqueous solvents.

TABLE II Rate constant (k)[a] and half-life ($t_{1/2}$) of ligand exchange reaction between $[Fe(phen)_3]^{2+}$ and $[Fe(DIP)_3]^{2+}$ in various solvents

	$[Fe(phen)_3]^{2+}$		$[Fe(DIP)_3]^{2+}$	
Solvent	$k[h^{-1}]$	$t_{1/2}$ [h]	$k[h^{-1}]$	$t_{1/2}$ [h]
Acetonitrile	17.8×10^{-3}	38.9	11.7×10^{-3}	59.2
Methanol	7.62×10^{-3}	91.2	4.10×10^{-3}	169
Acetone	71.3×10^{-3}	9.72	52.0×10^{-3}	13.3
Chloroform	30.9×10^{-3}	22.0	25.7×10^{-3}	27.0
Dichlormethane	30.0×10^{-3}	23.1	23.8×10^{-3}	29.1

[a] Defined as described in Table II.

Detailed results from the calculation of the rate constant at different pH's and in various solvents are given in Tables I and II.

RESULTS AND DISCUSSION

An example of a contour plot and chromatogram for the reaction mixture of $[Fe(phen)_3]^{2+}$ and $[Fe(DIP)_3]^{2+}$ is given in Figure 1. The chromatogram was taken one week after mixing at which the equilibrium between products and reactants was reached. This figure shows clearly that three additional peaks, *i.e.*, peaks 2, 3 and 4 appear. The small peak 2 belongs to 1,10-phenanthroline ligand which may arise from the dissociation/aquation of $[Fe(phen)_3]^{2+}$ due to nitrogen protonation of the ligand at the relatively low pH of the solution ($pH = 3$). At higher pH ($pH = 6$ and 8), no peak for the free phen ligand was observed in the chromatogram, suggesting that protonation of the nitrogen atom of the ligand probably did not occur. Peaks 3 and 4 correspond to mixed-ligand complexes formed by the ligand exchange reaction between $[Fe(phen)_3]^{2+}$ and $[Fe(DIP)_3]^{2+}$. This assignment is based on the existence of an absorption in the visible region (see contour plot) which is characteristic of the metal-to-ligand charge transfer (MLCT) band. To support this assignment, isolation of the mixed-ligand complexes from the ligand exchange reaction was carried out and the complexes obtained were identified by elemental analysis and electronic absorption spectroscopy. The results of elemental analyses support our conclusion and are presented in Table III.

The mixed-ligand complexes produced were fractionated by preparative HPLC using the conditions above except that $HClO_4$ was replaced by $LiClO_4$, followed by evaporation of acetonitrile and extraction of the complexes from the aqueous solution into chloroform. The chloroform solution was then evaporated on a rotary evaporator to give crystalline

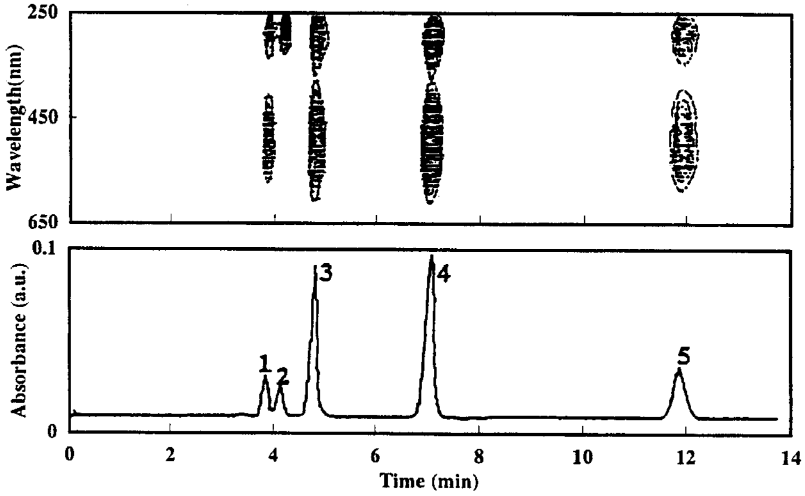


FIGURE 1 Contour plot and chromatogram of $[Fe(phen)_3]^{2+}$ and $[Fe(DIP)_3]^{2+}$ in a week after mixing: (1) $[Fe(phen)_3]^{2+}$, (2) phen, (3) $[Fe(phen)_2(DIP)]^{2+}$, (4) $[Fe(phen)(DIP)_2]^{2+}$ and (5) $[Fe(DIP)_3]^{2+}$. HPLC conditions; column: Inertsil ODS, mobile phase: $MeCN-H_2O$ (80/20, v/v) 0.06 M $NaClO_4$, flow rate: 0.8 ml/min.

TABLE III Analytical data of mixed-ligand complexes obtained by ligand exchange between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$

		Elemental analysis		
Complex	*HPLC*[a] R_t/[*min*]	%*C* (*Calcd.*)	%*N* (*Calcd.*)	%*H* (*Calcd.*)
$[Fe(phen)_2(DIP)](ClO_4)_2$	3.94	59.6 (59.2)	8.7 (8.4)	3.5 (3.5)
$[Ni(phen)_2(DIP)](ClO_4)_2 \cdot 5H_2O$	4.64	55.1 (55.4)	7.9 (8.1)	3.9 (4.0)
$[Fe(phen)(DIP)_2](ClO_4)_2$	5.89	65.5 (64.9)	7.8 (8.0)	3.7 (4.0)
$[Ni(phen)(DIP)_2](ClO_4)_2 \cdot 5H_2O$	6.93	59.4 (59.5)	6.8 (6.9)	4.1 (4.3)

[a] Eluent: CH_3CN-H_2O (80/20, v/v) containing 0.06 M $HClO_4$, column: Inertsil ODS, flow rate: 1.0 ml/min, R_t: retention time.

complexes. Electronic spectral studies show that the ligands, phen and DIP, have only one λ_{max} in the ultraviolet (UV) region at, respectively, 265 nm and 275 nm ascribed to an intraligand transition ($\pi \rightarrow \pi^*$, ILT). On the other hand, each mixed-ligand complex exhibits one λ_{max} and one shoulder in the UV region at 271 nm and 284 nm for both iron(II) and nickel(II) complexes due to ILT of phen and DIP contained in each complex. In addition, another intense absorption in the visible region at 517 nm for $[Fe(phen)_2(DIP)]^{2+}$ and at 525 nm for $[Fe(phen)(DIP)_2]^{2+}$ was also observed for iron(II) mixed-ligand complexes due to the metal-to-ligand charge transfer ($d \rightarrow \pi^*$, MLCT) [20, 21]. Upon coordination of phen and DIP to metal(II) ions, all the ILT bands are shifted to longer wavelengths. The MLCT absorption of the iron(II) complexes indicates a regular bathochromic shift of about 7 nm from that observed for *tris*-$[Fe(phen)_3]^{2+}$ as the number of phen ligands in the iron(II) complexes decreases. This supports the assumption that two additional peaks appearing between the peaks of the two complexes, *i.e.*, peaks 3 and 4 in Figure 1, are attributed to mixed-ligand complexes resulting from the ligand exchange between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$.

Effect of pH on the Ligand-Exchange Reaction

The effect of pH of the solution on ligand exchange has been studied by examining the characteristics of the ligand exchange reaction between two types of complexes at various pH's of the mixing solution, *i.e.*, pH = 0.5, 3.0, 6.0 and 8.0. Figure 2 shows the typical kinetic plots of peak area *vs.* reaction time where the ligand exchange between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ at pH = 6.0 was monitored by HPLC. Analogous trends in the ligand-exchange reaction are observed for pH = 3.0 and 8.0 of the mixing solution. The analysis of the kinetic data (Tab. I) revealed that the ligand-exchange reactions at pH = 3.0, 6.0 and 8.0 either for iron(II) or nickel(II) complexes take place at a similar rate. A comparison of the results obtained for iron(II) and nickel(II) complexes, however, indicates that in the case of nickel(II), the rate of ligand exchange is approximately two times slower than that observed for iron(II) complexes. In addition, our results show that the decreasing rate of the concentrations of both $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ at $pH < 3$ is faster than that found at pH = 3–8. However, the ligand-exchange reaction hardly proceeds at pH of the solution below 3. Only a small amount of $[Fe(DIP)_2(phen)]^{2+}$ was detected several days after the mixing, while $[Fe(phen)_2(DIP)]^{2+}$ was not. This observation suggests that the faster decrease in the concentrations of both $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ found when the pH of the solution is less than 3, it is not due to the ligand exchange reaction but due to the rapid dissociation of the complexes to yield the nitrogen-protonated free phen and DIP [22]. The protonation of phen and DIP ligands at one of their nitrogen atoms make it difficult for them to form complexes, *i.e.*, the formation of mixed-ligand complexes. This is the reason little or no mixed-ligand complexes are

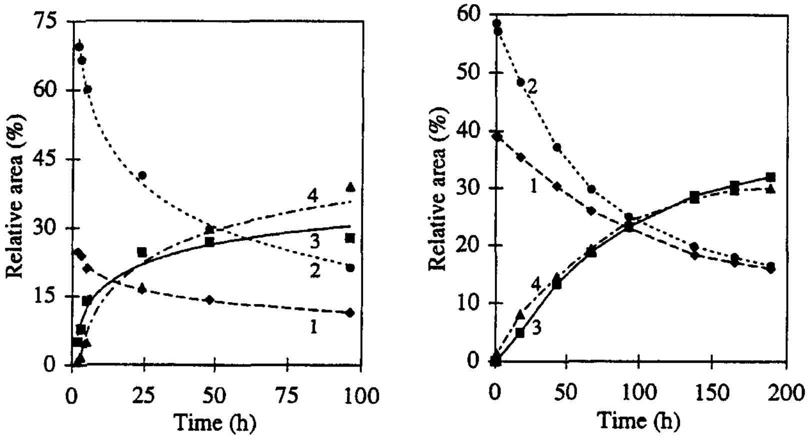
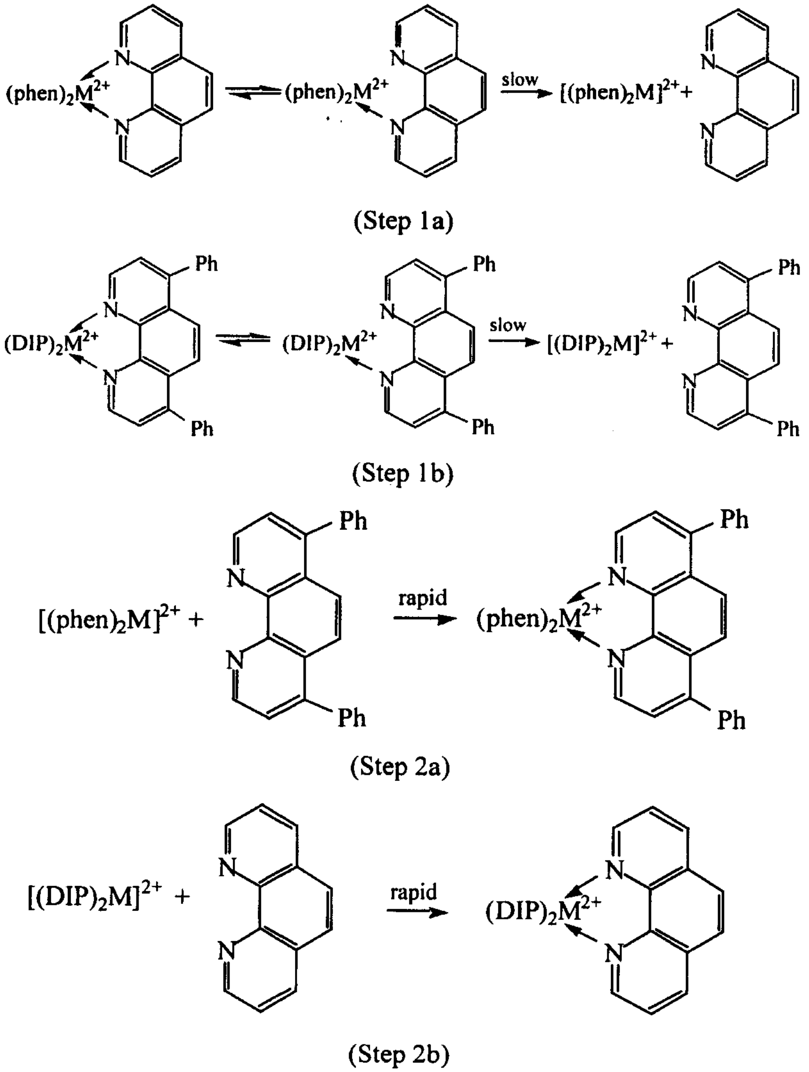


FIGURE 2 Typical time-dependence of ligand-exchange reaction between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ at $pH = 6.0$ monitored by HPLC: iron(II) complexes (left) and nickel(II) complexes (right): (1) $[M(phen)_3]^{2+}$, (2) $[M(DIP)_3]^{2+}$, (3) $[M(phen)_2(DIP)]^{2+}$ and (4) $[M(phen)(DIP)_2]^{2+}$.

detected when the solution of $pH < 3$ is employed although the decrease in reactant concentrations is faster than that in the pH range of 3–8. The detection of a small amount of $[M(phen)(DIP)_2]^{2+}$ indicates that this complex is more stable in acidic solution than $[M(phen)_2(DIP)]^{2+}$ complex.

That the ligand exchange reaction of nickel(II) complexes is approximately two times slower than that of iron(II) complexes may be explained in terms of the dissociation and/or racemization constants of the complexes. The dissociation process of the complexes presented in Scheme 1, Steps 1a and 1b, seem to be more reasonable because releasing one ligand from the complexes is required in a ligand exchange reaction. It has been reported that $[Ni(phen)_3]^{2+}$ dissociates and racemizes ($k_{diss} = 7.5 \times 10^{-6}\,s^{-1}$, $k_{rac} = 9.4 \times 10^{-6}\,s^{-1}$, in water at 25°C) slower than does $[Fe(phen)_3]^{2+}$ ($k_{diss} = 7.0 \times 10^{-5}\,s^{-1}$, $k_{rac} = 6.5 \times 10^{-4}\,s^{-1}$) [11,23]. On the other hand, the decreasing rate of $[Fe(phen)_3]^{2+}$ concentration due to ligand exchange at $pH = 6.0$, for example, is $2.2 \times 10^{-6}\,s^{-1}$ (see Tab. I). This value is somewhat lower than the rate of dissociation constant of $[Fe(phen)_3]^{2+}$ in water at 25°C as mentioned above. However, it is still comparable even though the solvents used in the experiments are different. The kind of solvents used may lead to different rate constants, indicating that the loss of one ligand molecule from the *tris*-complex likely becomes the rate-determining step for the ligand-exchange reaction and thus the ligand substitution reaction proceeds in a dissociative mechanism. Scheme 1 gives



SCHEME 1

one of the possible mechanisms of the ligand exchange reaction between $[M(phen)_3]^{2+}$ and $[M(DIP)_3]^{2+}$ that yields mixed-ligand complexes. It should be noted, however, that the mechanism is simplified only to describe how the mixed-ligand complexes are formed. The real mechanism could be very complicated because the releasing groups, *i.e.*, phen and DIP ligands might re-react with intermediates $[M(phen)_2]^{2+}$ and $[M(DIP)_2]^{2+}$ to form *tris*-complexes in addition to mixed-ligand complexes. This assumption is supported by our results from plotting reaction time (t) *vs.* $\ln C$ (first-order) or $1/C$ (second-order) where C is the increasing concentrations of the products, *i.e.* $[M(phen)_2(DIP)]^{2+}$ or $[M(phen)(DIP)_2]^{2+}$, which gives non-linear curves. This indicates that the last two reactions expressed in Scheme 1, Steps 2a and 2b are neither simple first-order nor second-order reactions. The typical chromatograms obtained in the course of the ligand-exchange reaction are presented in Figure 3. The chromatograms show clearly the decrease in the concentrations of $[Ni(phen)_3]^{2+}$ and $[Ni(DIP)_3]^{2+}$ (peaks 1 and 4) as well as the increase in the concentrations of mixed-ligand complexes $[Ni(phen)_2(DIP)]^{2+}$ and $[Ni(phen)(DIP)_2]^{2+}$ (peaks 2 and 3) after mixing of the complexes.

Effect of Solvents on Ligand-Exchange Reaction

The effect of solvents on the ligand-exchange reaction between $[Fe(phen)_3]^{2+}$ and $[Fe(DIP)_3]^{2+}$ is studied by examining the reaction in various solvents. Five solvents have been used in the experiments, *i.e.*, acetonitrile, methanol, acetone, dichloromethane and chloroform. The selection of the solvents was based on the large solubility of both complexes. The kinetic plots of peak area *vs.* reaction time obtained from HPLC monitoring of the ligand exchange reaction in acetone and methanol are

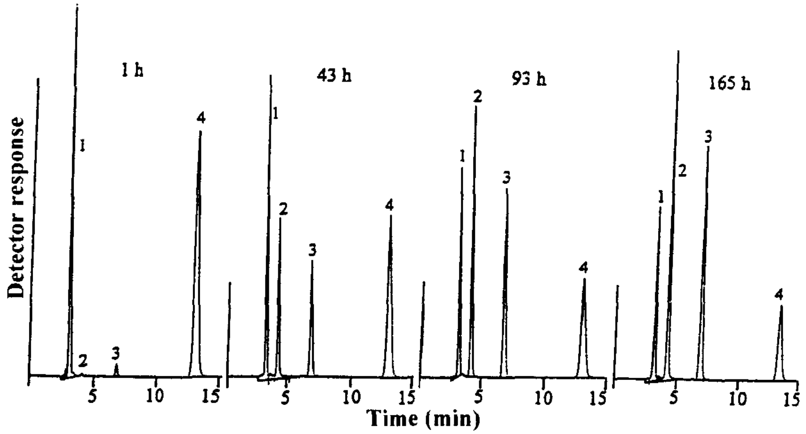


FIGURE 3 Chromatographic profiles obtained in the course of ligand-exchange reaction between $[Ni(phen)_3]^{2+}$ and $[Ni(DIP)_3]^{2+}$. (1) $[Ni(phen)_3]^{2+}$, (2) $[Ni(phen)_2(DIP)]^{2+}$, (3) $[Ni(phen)(DIP)_2]^{2+}$ and (4) $[Ni(DIP)_3]^{2+}$. HPLC conditions; column: Inertsil ODS, mobile phase: $MeCN-H_2O$ (80/20, v/v) 0.06 M $NaClO_4$, flow rate: 1.0 ml/min, detection wavelength: 284 nm.

given in Figure 4 and the results of kinetic analysis are presented in Table II. An examination of Table II revealed that the ligand exchange reaction of the iron(II) complexes is accelerated by solvent in the order: $(CH_3)_2CO > CHCl_3 \geq CH_2Cl_2 > CH_3CN > CH_3OH$. This order reflects firmly the degree of solubility of both complexes in the solvents used. However, the mechanism in which the solvents accelerate the reaction is still unclear especially for CH_3Cl and CH_2Cl_2. In the case of $(CH_3)_2CO$, CH_3CN and CH_3OH, their enhancement effect on ligand exchange may be explained by their participation in the dissociation process of the complexes (Scheme 1 Steps 1a and 1b), *i.e.*, their coordination to intermediate *bis*-complexes $[M(phen)_2]^{2+}$ and $[M(DIP)_2]^{2+}$ (Eqs. 1a and 1b).

$$[M(phen)_2]^{2+} \xrightarrow{\text{solvent}} [M(phen)_2(solvent)_2]^{2+} \qquad (1a)$$

$$[M(DIP)_2]^{2+} \xrightarrow{\text{solvent}} [M(DIP)_2(solvent)_2]^{2+} \qquad (1b)$$

The two solvent molecules in the intermediate complexes are then immediately replaced in another dissociative mechanism by free ligands such as phen or DIP to produce mixed-ligand complexes containing phen and DIP. The enhancement order of the solvents in the ligand-exchange reaction; $(CH_3)_2CO > CH_3CN > CH_3OH$ is consistent with the coordination capability of the solvents and thus supports the above explanation. Such a role of acetone in the synthesis of mixed-ligand complexes involving

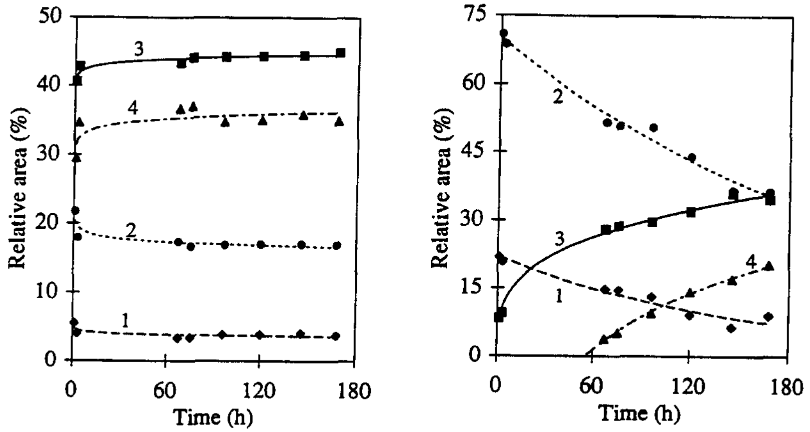


FIGURE 4 Typical time-dependence of ligand-exchange reaction between $[Fe(phen)_3]^{2+}$ and $[Fe(DIP)_3]^{2+}$ in acetone (left) and in methanol (right): (1) $[Fe(phen)_3]^{2+}$, (2) $[Fe(DIP)_3]^{2+}$, (3) $[Fe(phen)_2(DIP)]^{2+}$ and (4) $[Fe(phen)(DIP)_2]^{2+}$.

2,2′-bipyridine and phosphine also has been reported [24]. In conclusion, it has been demonstrated that the ligand exchange reaction is enhanced by solvent in the order: $(CH_3)_2CO > CHCl_3 \geq CH_2Cl_2 > CH_3CN > CH_3OH$, in accordance with the degree of solubility of the complexes in the solvents.

Acknowledgment

The first author (M) acknowledges The Hitachi Scholarship Foundation, Tokyo, Japan for financial support.

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