

The Nucleophilic Ring Substitutions of Asymmetrical Tetradentate Schiff Base Complexes of Nickel(II) and Copper(II)

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Seven new complexes where the chelate ring was nucleophilically substituted were synthesized by the reactions of asymmetrical tetradentate Schiff base complexes of nickel(II) and copper(II) with benzenethiols and thioglycolic ethyl ester. They were characterized by means of elemental analyses, electronic and $^1\text{H-NMR}$ spectra. Kinetics of the nucleophilic ring-substitution reactions were spectrophotometrically studied in a benzene solution. A four-centered intermediate is proposed for the reactions.

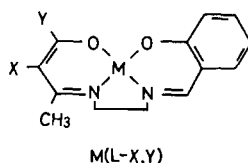


Fig. 1. Abbreviation of the Schiff base complexes: M is nickel(II) or copper(II); X is bromo, phenylthio, *p*-methylphenylthio, *p*-nitrophenylthio, or ethoxycarbonylmethylthio; Y is methyl or phenyl group, respectively.

Introduction

Although electrophilic ring-substitution reactions of metallo β -diketone and Schiff base complexes have been extensively studied from synthetic aspects [1–4], only a few studies have been reported on the reaction mechanism [5–7]. One of the reasons is that these complexes have two or more methine carbons in the chelate rings, which makes it difficult to study their kinetics. In the previous paper a series of asymmetrical tetradentate Schiff base complexes of nickel(II) and copper(II) which have only one methine carbon in their chelate ring was prepared, and their halogenation with *N*-chlorosuccinimide (NCS) was kinetically studied [7]. Furthermore, a few nucleophilic substitutions on the coordinated ligand of metallo β -diketone and tetradentate Schiff base complexes have been reported [8–10].

In the present paper, further conversion of the halogen-substituted methine carbon of the asymmetrical Schiff base complexes of nickel(II) and copper(II) was performed by nucleophiles such as benzenethiol, *p*-methylphenylthiol, *p*-nitrophenylthiol and thioglycolic ethyl ester. The kinetics of the reactions is also reported to elucidate the nucleophilic substitution mechanism. The abbreviation of the complexes used in this study is shown in Fig. 1.

Experimental

Syntheses

Bromo Derivatives

[*N*-(2-bromo-1-methyl-3-oxobutylidene)-*N'*-salicylideneethylenediaminato]copper(II), Cu(L-Br, Me) was prepared by the method reported before [7]; that is, the bromo derivative was prepared by the reaction of *N*-bromosuccinimide (NBS) and [*N*-(1-methyl-3-oxobutylidene)-*N'*-salicylideneethylenediaminato]copper(II), Cu(L-H, Me) which was prepared according to the method reported by Kusuka *et al.* [11]. The bromo derivative of nickel(II), Ni(L-Br, Me) was prepared by the reaction of nickel(II) acetate and the free ligand which was previously liberated from the copper(II) complex with hydrogen sulfide [7].

Phenylthio Derivatives

The dichloromethane solution (20 ml) of 0.36 g (3.3 mmol) benzenethiol was added dropwise to 50 ml of the dichloromethane solution of 1.2 g (3.0 mmol) Ni(L-Br, Me) below -5°C for 2 h. After filtration, the filtrate was concentrated under a reduced pressure. By the addition of adequate amounts of methanol to the filtrate, [*N*-(1-methyl-3-oxo-2-(phenylthio)butylidene)-*N'*-salicylideneethylenediaminato]nickel(II), Ni(L-SC₆H₅, Me) was precipitated, which was subsequently recrystallized from dichloromethane and a small amount of methanol.

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The other nickel(II) and copper(II) derivatives of benzenethiols were prepared in a similar manner.

Ethoxycarbonylmethylthio Derivatives

The dichloromethane solution (20 ml) of 0.40 g (3.3 mmol) thioglicolic ethyl ester was added dropwise to 50 ml of the dichloromethane solution of 1.2 g (3.0 mmol) Ni(L-Br, Me) below -10°C . The solution was left standing with stirring below -10°C for 2 h. After filtration, the filtrate was subsequently concentrated under reduced pressure, resulting in tarry precipitates. The tarry matter was then dissolved into adequate amounts of hexane, and the solution was left at room temperature overnight. The orange precipitates thus obtained were recrystallized from methanol. The derivative of Ni(L-Br, Ph) was prepared in a similar manner. In this case, the product was further purified by column chromatography on alumina.

Measurements

The solvents used for kinetic measurements were dehydrated on anhydrous calcium chloride and distilled under a reduced pressure. N-bromosuccinimide (NBS) was recrystallized from ethanol, and was dried under a reduced pressure. The rate was measured by the absorbance change with time by means of a Hitachi 215 spectrophotometer. The temperature was $20.0 \pm 0.1^{\circ}\text{C}$.

The $^1\text{H-NMR}$ spectra were recorded with a JEOL-MH 100 spectrophotometer at a frequency of 100 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard. The electronic spectra in solution were measured on a Hitachi 215 spectrophotometer.

Results and Discussion

Electronic and $^1\text{H-NMR}$ Spectra

The results of elemental analyses and yields are listed in Table I.

TABLE I. Analytical and Yields Data for the Nucleophilically Substituted Compounds^a.

Complex	Found (%)			Calcd (%)			Yields (%)
	C	H	N	C	H	N	
Ni(L-SC ₆ H ₅ , Me)	58.25	4.62	6.51	58.42	4.91	6.81	36
Ni(L-SC ₆ H ₄ NO ₂ , Me)	51.97	4.21	9.46	52.65	4.21	9.21	37
Ni(L-SC ₆ H ₄ CH ₃ , Me)	58.87	4.95	6.71	59.31	5.23	6.59	33
Ni(L-SC ₆ H ₄ NO ₂ , Ph)	57.68	4.23	7.95	57.93	4.09	8.11	49
Ni(L-SCH ₂ CO ₂ C ₂ H ₅ , Me)	51.02	5.27	6.53	51.33	5.28	6.65	18
Ni(L-SCH ₂ CO ₂ C ₂ H ₅ , Ph)	56.81	4.58	6.21	57.16	5.02	5.80	31
Cu(L-SC ₆ H ₄ NO ₂ , Me)	51.86	3.98	8.83	52.10	4.16	9.12	28

^aYields are mol percentages. SC₆H₅, SC₆H₄NO₂, SC₆H₄CH₃, and SCH₂CO₂C₂H₅ denote phenylthio, *p*-nitrophenylthio, *p*-methylphenylthio, and ethoxycarbonylmethylthio groups respectively.

In Table II, the data of electronic spectra in a benzene solution are shown. The copper(II) derivative shows the absorption band at 558 nm, which is assigned to the d_{z^2} or $d_{x^2-y^2}$ to d_{xy} transition according to the assignment brought about for Cu(L-H, Me) [11].

The nickel(II) derivatives also show the absorption bands arising from the $d-d$ transition at 540–550 nm, which is characteristic of square planar nickel(II) complexes. A few strong absorption bands of the copper(II) and nickel(II) complexes in the region of 300 to 460 nm are tentatively assigned to $\pi-\pi^*$ and charge transfer bands respectively [11].

The nickel(II) derivatives of benzenethiols and thioglicolic ethyl ester show $^1\text{H-NMR}$ signals of the nucleophilic reagents, indicating the displacement of bromine by the substituents (Table III). Furthermore, the nucleophilically ring-substituted derivatives of nickel(II) shift the $^1\text{H-NMR}$ signals of their methyl groups attached to the chelate ring to lower magnetic fields with respect to that (2.15 ppm) of the unsubstituted complex, Ni(L-H, Me). This may be caused from the deshielding effects by the ring current of the phenyl group and the magnetic anisotropy of the carbonyl groups respectively.

Although the nucleophilically ring-substituted compounds were obtained by the reaction of the Schiff base complexes with benzenethiols and thioglicolic ethyl ester, the nucleophiles such as thioalcohols, thioglicol and thioglicolic acid gave no substituted compounds because of the reduction of bromine to hydrogen on the methine carbon. The successful nucleophilic ring substitution may be significantly related to the reducing ability of sulfur in the nucleophiles.

Kinetics of the Nucleophilic Ring-Substitution Reactions

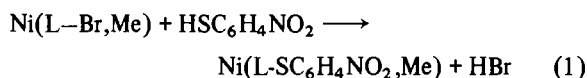
By the addition of *p*-nitrophenylthiol, HSC₆H₄NO₂, the spectrum of Ni(L-Br, Me) in a benzene solution changed with time, finally giving the spectrum of Ni(L-SC₆H₄NO₂, Me).

TABLE II. Electronic Data for the Nucleophilically Substituted Compounds in Benzene Solution.

Complex	λ max/nm (log ϵ) ^a				
Ni(L-SC ₆ H ₅ , Me)	336(3.84)	381(3.56)	420(3.47)	455 ^{sh} (3.37)	550 ^{sh} (2.18)
Ni(L-SC ₆ H ₄ NO ₂ , Me)	340(4.30)		410 ^{sh} (3.63)	450 ^{sh} (3.41)	544 ^{sh} (2.13)
Ni(L-SC ₆ H ₄ CH ₃ , Me)	333(4.08)	378(3.82)	418(3.71)	455 ^{sh} (3.63)	548 ^{sh} (2.18)
Ni(L-SC ₆ H ₄ NO ₂ , Ph)	341(4.37)		415 ^{sh} (3.86)	450 ^{sh} (3.55)	551(2.20)
Ni(L-SCH ₂ CO ₂ C ₂ H ₅ , Me)	337(3.81)	378(3.53)	420(3.45)	457 ^{sh} (3.32)	545(2.18)
Ni(L-SCH ₂ CO ₂ C ₂ H ₅ , Ph)	310 ^{sh} (4.09)	390 ^{sh} (3.72)	413(3.78)	455 ^{sh} (3.51)	553(3.28)
Cu(L-SC ₆ H ₄ NO ₂ , Me)	333(3.80)	390 ^{sh} (3.75)			558(2.15)

^aSh = shoulder.TABLE III. ¹H-NMR Data for the Nucleophilically Substituted Compounds of Nickel(II) in CDCl₃^a.

Complex	δ CH ₃	δ CH ₂	δ (aromatic and azomethine protons)
Ni(L-SC ₆ H ₅ , Me)	2.56(6H,d)	3.50–4.00(4H,m)	7.83–8.16(9H,m), 8.42(H,s)
Ni(L-SC ₆ H ₄ NO ₂ , Me)	2.50(6H,m)	3.50–4.01(4H,m)	7.83–8.49(7H,m), 9.00(2H,m)
Ni(L-SC ₆ H ₄ CH ₃ , Me)	2.60(9H,d)	3.50–3.93(4H,m)	7.83–7.99(8H,m), 8.32(H,s)
Ni(L-SC ₆ H ₄ NO ₂ , Ph)	2.53(3H,s)	3.66–3.93(4H,brs)	8.16–8.46(12H,brs), 9.02(2H,m)
Ni(L-SCH ₂ CO ₂ C ₂ H ₅ , Me)	1.42(3H,m)	3.30–3.76(6H,m)	7.16–7.82(5H,brm)
	2.54(6H,s)	4.55(2H,m)	
Ni(L-SCH ₂ CO ₂ C ₂ H ₅ , Ph)	1.39(3H,m)	3.30–3.80(6H,m)	7.10–8.51(10H,brm)
	2.57(3H,s)	4.46(2H,m)	

^aConfidence limits are ± 0.02 ppm. s = singlet, d = doublet, m = multiplet, and br = broad.

The rate of the reaction (1) was determined by the absorbance change at 430 nm by a pseudo first-order method. The plot of $-\ln(A_\infty - A_t)$ vs. time was linear for at least 80% completion; A_t and A_∞ represent the absorbance at time t and infinity respectively. From the slope, the pseudo first-order rate constant (k_{obsd}) was estimated to be $(6.8 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$. The rate was also measured at 460 nm. Both values were the same (within experimental error),

showing no wavelength-dependence of the rate. The value of k_{obsd} was proportional to the concentration of *p*-nitrophenylthiol, showing the first order with respect to the concentration of the nucleophile (Table IV).

Further experiments were performed to elucidate the reaction mechanism (Table IV), and the results were as follows: 1) The reaction of Ni(L-Cl, Me) and *p*-nitrophenylthiol was so slow that the rate constant could not be obtained. That is, polarizability of the halogen atom seems to be important for the nucleophilic substitution reactions. 2) The rate

TABLE IV. The Rate Constants of the Reactions of the Nickel(II) and Copper(II) Complexes with Benzenethiols in the Benzene Solution

Run	$k_{\text{obsd}}^a/10^{-3} \text{ s}^{-1}$	Conditions
1	5.5 ± 0.3	Ni(L-Br,Me) + HSC ₆ H ₄ NO ₂ ($2.5 \times 10^{-3}/\text{mol dm}^{-3}$)
2	6.8 ± 0.4	ibid ($3.0 \times 10^{-3}/\text{mol dm}^{-3}$)
3	7.5 ± 0.2	ibid ($3.5 \times 10^{-3}/\text{mol dm}^{-3}$)
4	9.1 ± 0.5	ibid ($4.0 \times 10^{-3}/\text{mol dm}^{-3}$)
	$k^b/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	
5	2.3 ± 0.2	Ni(L-Br,Me) + HSC ₆ H ₄ NO ₂
6	3.3 ± 0.4	Ni(L-Br,Ph) + HSC ₆ H ₄ NO ₂
7	4.2 ± 0.2	Ni(L-Br,Me) + HSC ₆ H ₅
8	5.2 ± 0.5	Ni(L-Br,Me) + HSC ₆ H ₄ CH ₃
9	13.1 ± 1.50	Cu(L-Br,Me) + HSC ₆ H ₄ NO ₂
10	0.16 ± 0.01	Ni(L-Br,Me) + HSC ₆ H ₄ NO ₂ with 10% triethylamine

^aThe first-order rate constants.^bThe second-order rate constants.

constant of the reaction for Ni(L-Br, Ph) was slightly larger than that for Ni(L-Br, Me) (Runs 5 and 6). The phenyl group decreases the electron density on the chelate ring, promoting the nucleophilic substitution on the methine carbon. 3) The complexes did not react with phenol in the same conditions used for the reaction with benzenethiol, consistent with the results reported to the reactions of metalloacetylacetonate complexes and phenol [8 and 9]. Thus, the polarizability of sulfur plays an important role in the nucleophilic ring-substitution reactions. Furthermore, the rate constant for *p*-nitrophenylthiol is smaller than those for benzenethiol and *p*-methylphenylthiol (Runs 7-9), indicating that the electron density on sulfur also affects the rate constant. 4) The rate constant for Cu(L-Br, Me) was almost six times that for Ni(L-Br, Me) (Run 9). In the case of the chlorination, the rate constant for Cu(L-H, Me) ($800 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) is also larger than that for Ni(L-H, Me) ($53 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) [7].

These large differences of the reaction rate constants between the copper(II) and nickel(II) complexes may not be caused from the electron-withdrawing effect of the metal(II) ions, because of their similar electronegativities. The copper(II) ion might form the NCS or benzenethiol adduct of the complex which promotes the chelate-ring substitution reaction. At the present stage, however, we have no satisfactory explanation for the effect of the central metal(II) ions on the rate constant. 5) The addition of triethylamine into the reaction solution decreased significantly the rate constant (Run 10). 6) Although the effects of solvents on the rate constant were examined, successful results could not be obtained because of the appearance of long induction periods by the addition of the polar solvents such as acetone, diethyl ether, and ethyl alcohol. 7) The kinetics for the reaction of Ni(L-Br, Me) and thio-glicolic ethyl ester also could not be performed because of the existence of side reactions such as the reduction of bromine and the decomposition of the complex.

Although oxygen of phenol and chlorine on the methine carbon of the complexes could not give the substituted compounds, sulfur and bromine pro-

moted the substitution reactions. From the above results, a four-centered system is proposed for an intermediate of the nucleophilic ring-substitution reaction.

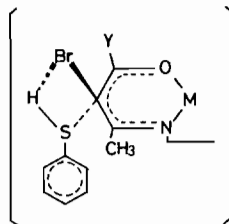


Fig. 2. The proposed intermediate.

The large polarizabilities of the atoms in the four-centered system might stabilize the intermediate, as was proposed for the reactions of metallo β -diketone complexes and benzenethiols [8]. Triethylamine might also make a hydrogen bonding with the hydrogen atom in the four-centered system, which destabilizes the intermediate. Further investigations, especially of the effects of the central metal ions and the solvent on the reaction rate, are needed to elucidate the detailed reaction mechanism.

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