Electrophilic Substitution Reactions on Methine Carbon of the Unsymmetrical Tetradentate Schiff Base and its Complexes with Nickel(II) and Copper(II)

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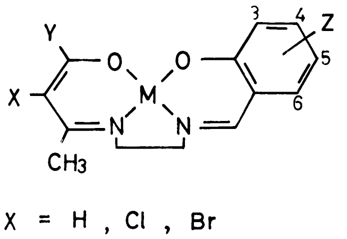
A number of unsymmetrical tetradentate Schiff base complexes of nickel(II) and copper(II) having only one methine carbon in the ligand were synthesized and characterized by means of UV and ^{1}H NMR spectra. The kinetic studies of the electrophilic substitution reactions on the methine carbon with *N*-halogenosuccinimide gave no support to an aromatic character of the chelate ring, being consistent with the results of ^{1}H NMR studies for the nickel(II) complexes.

Nature of the bonding in β-diketone metal complexes has been the subject of considerable controversy. A π-bonding between ligands and metal ion in the complexes was once proposed.[1—3)] However, an aromaticity of the chelate ring has been suspected on the basis of electronic spectral and ^{1}H NMR data.[4)] Collman and his coworkers subsequently reported various replacements of methine protons of these complexes by electrophiles such as bromine, iodine, *N*-halogenosuccinimide, nitro derivatives, acyl derivatives, and sulfur, suggesting the aromatic character of the chelate ring.[5)] Furthermore electrophilic substitution reactions on the chelate ring have been reported for mixed ligand β-diketone complexes of cobalt(III),[6)] and tetradentate Schiff base complexes of nickel(II) and copper(II).[7—9)] Further replacement of the halogen-substituted methine carbon of the β-diketone and tetradentate Schiff base complexes were also carried out using benzenethiol and its derivatives as a nucleophile.[8,10,11)]

Although the reactions of coordinated ligands were considerably studied from the synthetic aspects, only a few studies have been reported on the reaction mechanism.[6,9,12)] One of the reasons is the presence of two or more methine carbons in the chelate rings, which makes it difficult to study the reaction kinetics. In the present paper, a series of nickel(II) and copper(II) complexes with only one methine carbon in their chelate ring was prepared and the aromaticity of the chelate ring was studied by means of the ^{1}H NMR spectra and reaction kinetics of the electrophilic substitution on the methine carbon. The complexes used in the present study are shown in Fig. 1.



X = H , Cl , Br

Y = Me , Ph

Z = H , 3-OCH$_3$, 5-Br , 5-Cl

M = Ni(II) , Cu(II)

M(L-X,Y,Z)

Fig. 1. Abbreviation of the Schiff base complexes; Me and Ph denote methyl and phenyl groups, respectively.

Experimental

Complexes. [*N*-(1-Methyl-3-oxobutylidene)-*N*′-salicylideneethylenediaminato]copper(II), Cu(L-H, Me, H), was prepared by the method described before.[13)] Other derivatives of copper(II) were prepared according to the similar procedure to that for Cu(L-H, Me, H). However, the method was inapplicable to the preparation of the nickel(II) complex because of a great difficulty in separating the product from the by-products such as [*N,N*′-bis(1-methyl-3-oxobutylidene)ethylenediaminato]nickel(II) and (*N,N*′-disalicylideneethylenediaminato)nickel(II). Therefore, the nickel(II) complex, Ni(L-H, Me, H), was prepared by the reaction of nickel(II) acetate and a free ligand which was previously liberated from the copper(II) complex, Cu(L-H, Me, H). Hydrogen sulfide was bubbled through a chloroform solution(50 ml) of 1.0 g (3.2 mmol) Cu(L-H, Me, H) at room temperature for 20 min. After filtering off copper(II) sulfide, active charcoal was added to the filtrate, and the mixture was stirred for several min. After filtering off charcoal, tarry crude precipitates of the free ligand were obtained by concentrating the filtrate under a reduced pressure. The pale yellowish white crystals of the free ligand were subsequently recrystallized from cyclohexane. The nickel(II) complex was precipitated after standing a methanol solution(30 ml) of 0.74 g (3.0 mmol) free ligand and 0.75 g (3.0 mmol) nickel(II) acetate tetrahydrate at room temperature for 30 min. Then, the bright brown crystals of the nickel(II) complex were recrystallized from dichloromethane added with a small amount of methanol. The other nickel(II) complexes were prepared by the reactions of nickel(II) acetate tetrahydrate and the free ligands which were liberated from the corresponding copper(II) complexes.

Halogen Derivatives. *N*-Chlorosuccinimide (CSI) (0.44 g, 3.3 mmol) was added to 30 ml of the dichloromethane solution of 0.91 g (3.0 mmol) Ni(L-H, Me, H), which was stirred at room temperature for 20 min. After concentrating the solution under a reduced pressure, [*N*-(2-chloro-1-methyl-3-oxobutylidene)-*N*′-salicylideneethylenediaminato]nickel(II), Ni (L-Cl, Me, H), was precipitated by the addition of an adequate amount of methanol. The brown crystals were subsequently recrystallized from acetone. The other chloro derivatives were also prepared according to the similar method described above. Bromo derivatives of the nickel(II) complexes were prepared using *N*-bromosuccinimide (BSI) instead of CSI (the reaction temperature was maintained below −5 °C). The halogen derivatives of the copper(II) complexes were prepared using a similar method to the nickel(II) complexes. The chlorination of the free ligand was performed by adding 0.88 g (6.6 mmol) CSI to the 50 ml dichloromethane solution of 1.5 g (6.0 mmol) (L-H, Me, H), and was left at room temperature for 20 min. After evaporation of the solvent, the precipitates remained were dissolved in 30 ml methanol, and an adequate amount of water was added to the solution. Then, the pale yellowish white precipitates were obtained, and subsequently recrystallized from cyclohexane.

Kinetic Measurements. *N*-Chlorosuccinimide and *N*-bromosuccinimide were recrystallized from ethanol, and dried under a reduced pressure. The solvents used for kinetic measurements were dehydrated on anhydrous calcium chloride and distilled under a reduced pressure. The reaction rate was measured by the absorbance change with time on a Hitachi 215 spectrophotometer. The temperature was kept at 20.0±0.1 °C.

Other Measurements. The ^{1}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}H NMR Spectra of the Complexes. The results of elemental analyses and yields of the complexes are listed in Table 1.

In Table 2, the electronic spectral data in benzene solutions are given. Nickel(II) complexes (**1**—**20**) show the d-d absorption bands at 550—570 nm which are characteristic of a square planar nickel(II) complex. The Ni(L-X, Ph, Z) complexes (**5**—**8** and **13**—**16**) show the d-d bands at longer wavelengths than Ni(L-X, Me, Z) (**1**—**4** and **9**—**12**). This lower-energy shift may be attributed to an electron-withdrawing effect of a phenyl group which weakens the in-plane crystal field. The 5-chloro and 5-bromo derivatives show little shift of the d-d bands, whereas the 3-methoxy derivatives (**4**, **8**, **12**, and **20**) shift the bands somewhat to longer wavelengths compared with the unsubstituted complexes (**1**, **5**, **9**, **13**, and **17**). The lower-energy shift in the methoxy derivatives may also be attributed to the electron-withdrawing effect of the methoxyl group. On the other hand, the d-d bands (560 nm) of the copper(II) complexes (**21**—**26**) show little shift. The π-π^* absorption bands in 310 to 350 nm have the following characteristic points; 1) the X substituents such as chlorine and bromine of the nickel(II) complexes (**9** and **17**) shift the bands to shorter wavelengths than Ni(L-H, Me, H) (**1**), whereas the Z substituents (**2**—**4**) to longer wavelengths. 2) In the copper(II) complexes, on the contrary, the X substituents (**24** and **25**) shift the bands to longer wavelengths, and the Z substituents scarcely shift the bands (**22** and **23**) compared with Cu(L-H, Me, H) (**21**). That is, the effect of copper(II) on the π-system of the chelate ring is different from that of nickel(II). Further studies will be performed on the effect of other metal ions on the π-π^* absorption bands.

The ^{1}H NMR data are listed in Table 3. The ^{1}H NMR signals arising from the methine proton disappear in the halogen derivatives, indicating the replacement of the methine proton with the substituents. The ^{1}H

Table 1. Elemental analyses and yields of the complexes

No.	Complex	Found/(%)			Calcd/(%)			Yield a)
		C	H	N	C	H	N	%
1	Ni(L-H, Me, H)	55.52	5.26	9.32	55.49	5.33	9.25	68
2	Ni(L-H, Me, Cl)	49.86	4.53	8.49	49.82	4.49	8.30	62
3	Ni(L-H, Me, Br)	43.65	3.75	7.31	44.02	3.97	7.34	58
4	Ni(L-H, Me, OCH$_3$)	54.09	5.44	8.42	54.09	5.46	8.41	61
5	Ni(L-H, Ph, H)	62.64	4.95	7.69	62.50	4.98	7.67	30
6	Ni(L-H, Ph, Cl)	56.64	4.40	6.69	57.11	4.30	7.01	15
7	Ni(L-H, Ph, Br)	51.41	3.90	6.13	51.39	3.87	6.31	45
8	Ni(L-H, Ph, OCH$_3$)	60.40	5.07	6.81	60.79	5.11	7.09	53
9	Ni(L-Cl, Me, H)	49.76	4.37	8.26	49.83	4.49	8.30	42
10	Ni(L-Cl, Me, Cl)	44.92	3.52	7.43	45.21	3.80	7.53	44
11	Ni(L-Cl, Me, Br)	40.18	3.30	6.69	40.38	3.40	6.73	58
12	Ni(L-Cl, Me, OCH$_3$)	48.78	4.92	7.33	49.02	4.67	7.62	70
13	Ni(L-Cl, Ph, H)	56.89	4.20	6.94	57.11	4.30	7.01	62
14	Ni(L-Cl, Ph, Cl)	52.55	3.71	6.40	52.58	3.72	6.46	63
15	Ni(L-Cl, Ph, Br)	47.59	3.36	5.43	47.69	3.38	5.86	67
16	Ni(L-Cl, Ph, OCH$_3$)	55.78	4.49	6.37	55.92	4.47	6.52	83
17	Ni(L-Br, Me, H)	44.04	3.72	7.41	44.02	3.97	7.34	30
18	Ni(L-Br, Me, Cl)	39.92	3.13	6.32	40.38	3.40	6.73	44
19	Ni(L-Br, Me, Br)	36.29	3.11	6.32	36.49	3.07	6.08	35
20	Ni(L-Br, Me, OCH$_3$)	43.65	3.94	6.63	43.73	4.17	6.80	55
21	Cu(L-H, Me, H)	54.95	5.15	9.23	54.62	5.25	9.10	63
22	Cu(L-H, Me, Br)	43.41	3.55	6.89	43.47	3.93	7.24	52
23	Cu(L-H, Me, OCH$_3$)	53.10	5.45	8.03	53.32	5.38	8.29	60
24	Cu(L-Cl, Me, H)	49.17	4.25	8.21	49.12	4.43	8.19	56
25	Cu(L-Br, Me, H)	42.98	3.85	7.08	43.47	3.93	7.24	28
26	Cu(L-Cl, Me, Br)	39.41	3.11	6.24	39.92	3.36	6.65	34
27	(L-H, Me, H)	68.03	7.45	11.14	68.26	7.38	11.37	76
28	(L-Cl, Me, H)	59.65	6.02	9.71	59.89	6.12	9.97	26

a) Yields are in molar percentages.

NMR signals of the methyl groups are largely shifted to lower magnetic fields in the order of X=H, Cl, and Br derivatives of nickel(II). This tendency is attributable to the magnetic anisotropic effect of halogen rather than to its inductive effect.

Aromaticity of the Chelate Rings. Nature of the chelate-ring bonding of β-diketone complexes has called considerable attention for a long time. In 1945, Calvin *et al.* proposed the conjugated system of type II for the chelate-ring bonding of the complexes.[1]

TABLE 2. ELECTRONIC SPECTRA OF THE COMPLEXES IN BENZENE

No.	M(L-X, Y, Z)	λ max/nm(log ε)				
1	Ni(L-H, Me, H)	340(3.87)	370^{sh}(3.62)	417(3.40)	452^{sh}(3.27)	555(2.01)
2	Ni(L-H, Me, Cl)	351(3.93)	375^{sh}(3.69)	432(3.40)	462^{sh}(3.34)	555^{sh}(2.19)
3	Ni(L-H, Me, Br)	352(4.00)	390(3.68)	419(3.58)	460^{sh}(3.38)	560(2.73)
4	Ni(L-H, Me, OCH_3)	352(3.95)	375(3.70)	427(3.43)	465^{sh}(3.30)	562(2.21)
5	Ni(L-H, Ph, H)	311(4.20)		414(3.83)	455^{sh}(3.54)	562(2.21)
6	Ni(L-H, Ph, Cl)	308(4.17)		408(3.81)	480^{sh}(3.26)	557^{sh}(2.26)
7	Ni(L-H, Ph, Br)	307(4.13)		407(3.98)	473^{sh}(3.30)	560^{sh}(2.29)
8	Ni(L-H, Ph, OCH_3)	315(4.10)		417(3.77)	456^{sh}(3.48)	564(2.18)
9	Ni(L-Cl, Me, H)	333(3.85)	393(3.69)	422(3.66)	458^{sh}(3.37)	564(2.18)
10	Ni(L-Cl, Me, Cl)	342(3.87)	387(3.65)	427(3.46)	465^{sh}(3.36)	565(2.20)
11	Ni(L-Cl, Me, Br)	342(3.82)	387(3.72)	426(3.51)	470^{sh}(3.32)	565(2.73)
12	Ni(L-Cl, Me, OCH_3)	337(3.87)	390(3.64)	420(3.49)	464^{sh}(3.26)	574(2.15)
13	Ni(L-Cl, Ph, H)	315(4.09)		413(3.77)	455^{sh}(3.46)	569(2.20)
14	Ni(L-Cl, Ph, Cl)	312(4.05)		406(3.76)	472^{sh}(3.29)	566(2.32)
15	Ni(L-Cl, Ph, Br)	312(4.12)		406(3.73)	475^{sh}(3.25)	566(2.25)
16	Ni(L-Cl, Ph, OCH_3)	318(4.09)		415(3.71)	455^{sh}(3.41)	576(2.16)
17	Ni(L-Br, Me, H)	332(3.81)	391(3.62)	422(3.57)	460^{sh}(3.35)	560(2.15)
18	Ni(L-Br, Me, Cl)	342(3.76)	387(3.61)	427(3.42)	466^{sh}(3.30)	557^{sh}(2.16)
19	Ni(L-Br, Me, Br)	342(3.82)	387(3.67)	427(3.49)	466^{sh}(3.25)	560(2.18)
20	Ni(L-Br, Me, OCH_3)	338(3.76)	391(3.63)	422(3.48)	466^{sh}(3.25)	570(2.18)
21	Cu(L-H, Me, H)	332(4.17)	393(3.69)			560(2.48)
22	Cu(L-H, Me, Br)	333(4.23)	401(3.67)			562(2.63)
23	Cu(L-H, Me, OCH_3)	333(4.23)	401(3.68)			560(2.63)
24	Cu(L-Cl, Me, H)	345(4.13)	393(3.66)			560(2.48)
25	Cu(L-Br, Me, H)	345(4.11)	393(3.63)			560(2.49)
26	Cu(L-Cl, Me, Br)	347(4.04)	403(3.61)			560(2.48)
27	(L-H, Me, H)	311(4.27)				
28	(L-Cl, Me, H)	330(4.22)				

Sh=Shoulder.

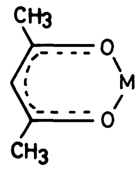
TABLE 3. ^1H NMR SPECTRA OF THE NICKEL (II) COMPLEXES IN CHLOROFORM-*d* (PPM)

No.	Complex	δ CH_3	δ CH_2	δ OCH_3	δ CH	δ (aromatic and azomethine protons)
1	Ni(L-H, Me, H)	2.15(6H, d)	3.33—3.53(2H, m) 3.66—3.83(2H, m)		5.51(H, s)	7.29—8.32(5H, m)
2	Ni(L-H, Me, Cl)	2.13(6H, d)	3.33—3.83(2H, m) 3.65—3.80(2H, m)		5.51(H, s)	7.59—8.25(4H, m)
3	Ni(L-H, Me, Br)	2.13(6H, d)	3.14—3.50(2H, m) 3.66—3.83(2H, m)		5.50(H, s)	7.32—8.25(4H, m)
4	Ni(L-H, Me, OCH_3)	2.15(6H, d)	3.33—3.50(2H, m) 3.66—3.86(2H, m)	4.16(3H, s)	5.51(H, s)	7.33—7.49(3H, m) 8.28(H, s)
5	Ni(L-H, Ph, H)	2.13(3H, s)	3.40—3.60(2H, t) 3.70—3.93(2H, t)		6.22(H, s)	7.19—7.76(4H, m) 8.12—8.61(6H, m)
6	Ni(L-H, Ph, Cl)	2.11(3H, s)	3.40—3.63(2H, m) 3.76—3.96(2H, m)		6.24(H, s)	7.56—8.03(3H, m) 8.12—8.58(6H, m)
7	Ni(L-H, Ph, Br)	2.10(3H, s)	3.40—3.63(2H, m) 3.76—3.96(2H, m)		6.23(H, s)	7.49—7.99(3H, m) 8.09—8.58(6H, m)
8	Ni(L-H, Ph, OCH_3)	2.15(3H, s)	3.43—3.66(2H, m) 3.73—3.96(2H, m)	4.26(3H, s)	6.24(H, s)	6.99—7.66(3H, m) 8.12—8.61(6H, m)
9	Ni(L-Cl, Me, H)	2.44(6H, s)	3.47—3.86(4H, m)			7.79—8.35(5H, m)
10	Ni(L-Cl, Me, Cl)	2.40(6H, d)	3.47—3.83(4H, m)			7.59—7.99(3H, m) 8.16(H, s)
11	Ni(L-Cl, Me, Br)	2.40(6H, d)	3.53—3.82(4H, m)			7.49—8.03(3H, m) 8.23(H, s)
12	Ni(L-Cl, Me, OCH_3)	2.43(6H, d)	3.53—3.83(4H, m)	4.19(3H, s)		7.16—7.56(3H, m) 8.25(H, s)
13	Ni(L-Cl, Ph, H)[a]	2.46(3H, s)	3.50—3.90(4H, m)			7.16—7.66(3H, m) 8.23—8.42(6H, m)

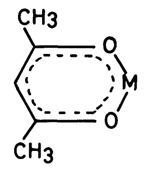
Table 3. (Continue)

No.	Complex	δ CH$_3$	δ CH$_2$	δ OCH$_3$	δ CH	δ (aromatic and azomethine protons)
16	Ni(L-Cl, Ph, OCH$_3$)[a]	2.51(3H, s)	3.53—3.80(4H, m)	3.80(3H, s)		7.16—7.66(3H, m) 8.33(6H, brs)
17	Ni(L-Br, Me, H)	2.51(6H, d)	3.53—3.83(4H, m)			7.72—8.16(4H, m) 8.25(H, s)
18	Ni(L-Br, Me, Cl)	2.50(6H, s)	3.50—3.96(4H, m)			7.66—7.99(3H, m) 8.24(H, s)
19	Ni(L-Br, Me, Br)	2.53(6H, s)	3.50—3.90(4H, m)			7.99—8.33(4H, m)
20	Ni(L-Br, Me, OCH$_3$)	2.53(6H, s)	3.50—3.83(4H, m)	4.23(3H, s)		7.16—7.66(3H, m) 8.46(H, s)
27	(L-H, Me, H)	2.05(6H, d)	3.76—4.13(4H, m)		5.31(H, s)	7.26—7.92(4H, m) 9.08(H, s)
28	(L-Cl, Me, H)	2.34(6H, d)	3.89—4.09(4H, m)			7.33—7.99(4H, m) 9.08(H, s)

Confidence limits are ±0.02 ppm. a) in 1, 1, 2, 2-tetrachloroethane-d_2. s=singlet, d=doublet, t=triplet, m =multiplet, and br=broad. The ^{1}H NMR spectra of Ni(L-Cl, Ph, Cl) and Ni(L-Cl, Ph, Br) were not obtained because of their poor solubilities.



(I)



(II)

Barnum also suggested the significant π-bonding between the ligands and the metal ion on the basis of electronic spectra.[2] Further, Nakamoto suggested from the results of IR spectra that acetylacetone complexes of nickel(II), copper(II), and palladium(II) have the structure of type (II), although those of zinc(II) and cobalt(II) have that of type (I).[3] However, Cotton *et al.* pointed out that the aromaticity was unreasonable on the basis of the symmetry and energy of the metal orbitals available for the π-bonding.[4] On the other hand, Collman and his coworkers have studied the numerous electrophilic substitution reactions on the chelate rings, which support the conjugate system of type (II).[5] They also reported the quasiaromatic character of the chelate ring from the ^{1}H NMR spectra of diamagnetic cobalt(III) and rhodium(III) complexes with the mixed ligands of acethylacetone and its derivatives.[14]

To examine the quasiaromatic character of the chelate ring of Ni(L-H, Y, Z), we investigated the effect of the Z groups on the ^{1}H NMR signals of the methine proton (Table 3). If the chelate ring had the quasiaromaticity, the electron density of the methine proton is expected to change with the Z groups. In a series of the complexes with the methyl substituents at position Y, Ni(L-H, Me, Z), the methine signals are observed at 5.51 (Z=H), 5.51 (Cl), 5.50 (Br), and 5.51 ppm (OCH$_3$), respectively. For Ni(L-H, Ph, Z), the signals appear at 6.22 (Z=H), 6.24 (Cl), 6.23 (Br), and 6.24 ppm (OCH$_3$). These facts show that the effect of the Z substituents is little on the ^{1}H NMR signals of the methine proton, and this agrees with the ^{1}H NMR data investigated for a broad range of diamagnetic metal complexes of acetylacetone; the metal ions do not significantly affect the shift of the methine-proton signals.[4] Therefore, the ^{1}H NMR data seem to give no support for an aromaticity of the nickel(II) chelate-ring of the Schiff base complexes such as shown in aromatic compounds.

Kinetics of Electrophilic Ring-substitution Reactions. By the addition of *N*-chlorosuccinimide, the spectrum

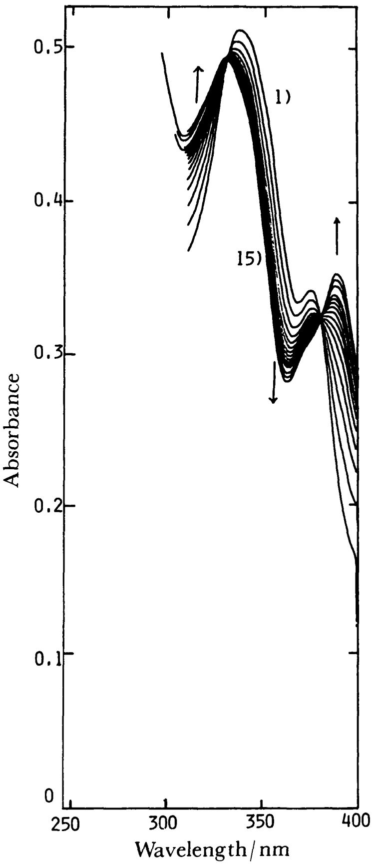


Fig. 2. Spectra changes during the reaction of Ni(L-H, Me, H) with CSI in the benzene solution at 20 °C; [Ni(L-H, Me, H)]$_0$=7.48×10^{-5} mol dm^{-3}, [CSI]$_0$=1.05×10^{-4} mol dm^{-3}: 1) 40 s, 2) 1 min 40 s, 3) 2 min 40 s, 7) 6 min 40 s, 11) 10 min 40 s, 13) 15 min 40 s, 14) 20 min 40 s, and 15) 30 min 40 s, after the reaction.

Table 4. The rate constants of the reactions of the complexes with CSI in a benzene solution

Run	$k/10^2\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$	Conditions		
1	0.53 ± 0.03	Ni(L-H, Me, H)	+	CSI
2	0.51 ± 0.04	same reactants with a few mg of the scavenger		
3	0.30 ± 0.02	Ni(L-H, Ph, H)	+	CSI
4	0.21 ± 0.05	Ni(L-H, Me, Cl)	+	CSI
5	0.25 ± 0.03	Ni(L-H, Me, Br)	+	CSI
6	0.55 ± 0.04	Ni(L-H, Me, OCH_3)	+	CSI
7	8.0 ± 1.2	Cu(L-H, Me, H)	+	CSI
8	1.1 ± 0.2	(L-H, Me, H)	+	CSI

Isosbestic points for the reactions of the copper(II) complex and the free ligand with CSI are at 337 and 324 nm, respectively. $[\text{complex}]_0=4.4\times10^{-5}$—$7.5\times10^{-5}\,\mathrm{mol\,dm^{-3}}$; $[\text{CSI}]_0=1.05\times10^{-4}\,\mathrm{mol\,dm^{-3}}$; temp$=20.0\pm0.1\,°\mathrm{C}$.

of Ni(L-H, Me, H) in the benzene solution changed to that of Ni(L-Cl, Me, H) with isosbestic points at 334 and 380 nm (Fig. 2). The existence of the isosbestic points clearly indicates that only the following reaction occurs:

Ni(L-H, Me, H)+CSI→Ni(L-Cl, Me, H)+succinimide. (1)

Thus, the rate of reaction (1) is determined by an absorbance change at 393 nm. The second-order plot of $(a-b)^{-1}\ln[b(A_t-A_\infty)/\{b(A_0-A_\infty)-a(A_0-A_t)\}]$ *versus* time is linear for at least 90% completion, a and b being intial concentrations of Ni(L-H, Me, H) and CSI. A_0, A_t, and A_∞ represent the absorbances at the beginning, time *t*, and infinity, respectively. From the slope, the rate constant was estimated to be $(5.3\pm0.3)\times10/\mathrm{mol^{-1}\,dm^3\,s^{-1}}$. The rate was also measured at 340 nm. The rate constant, $(5.1\pm0.4)\times10/\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, agreed with that obtained at 393 nm within an error, showing no wavelength dependence of the rate. The other rate constants were also obtained in a similar manner to that described above.

Further experiments were performed to elucidate the reaction mechanism (Table 4, Figs. 3 and 4), and the results are as follows: 1) A few mg of 2,6-di-*t*-butylphenol were added into the CSI solution and the solution was subsequently mixed with the Ni(L-H, Me, H) solution. The rate constant of the reaction (Run 2) was the same as that without scavenger (Run 1), which excludes a radical mechanism consistent with the result of the chlorination of [*N*,*N*′-bis(4,4,4-trifluoro-1-methyl-3-oxobutylidene)ethylenediaminato]nickel(II), Ni(tfac$_2$en), with CSI.[9] As shown in Fig. 3, the rate constant increased with the amount of dichloromethane added to the benzene solution. It is known that the reaction of CSI involves the radical mechanism in crystals or in solvents such as carbon tetrachloride and cyclohexane, but involves an ionic mechanism in solvents such as 1,1,2,2-tetrachloroethane and acetonitrile.[15,16] Thus, the above solvent effect observed supports the ionic mechanism. On the other hand, the rate constant decreased slightly by the addition of acetone and remarkably by ethyl ether. It has been reported that acetone and ethyl ether react with BSI to exchange α-hydrogen with bromine.[16] Thus, the addition of the solvents must decrease the concentration of CSI, resulting in the decrease of the rate constant; 2) The rate constant of the chlorination of Ni(L-H, Me, H) (Run 1) was almost the same as those of Ni(L-H, Me, Cl), and Ni(L-H, Me, Br) (Runs 3—5); 3) The rate constant of bromination with *N*-bromosuccinimide was larger than that of chlorination (the rate of bromination was so fast that the rate constant could not be determined). The smaller electron negativity of bromine may produce the cationic bromine more easily from BSI than the cationic chlorine from CSI; 4) The addition of triethylamine $(3.0\times10^{-5}/\mathrm{mol\,dm^{-3}})$ inhibited extreamly the reaction presumably because of the reaction with CSI;[16] 5) As is shown in Fig. 4, the addition of alcohols remarkably increased the

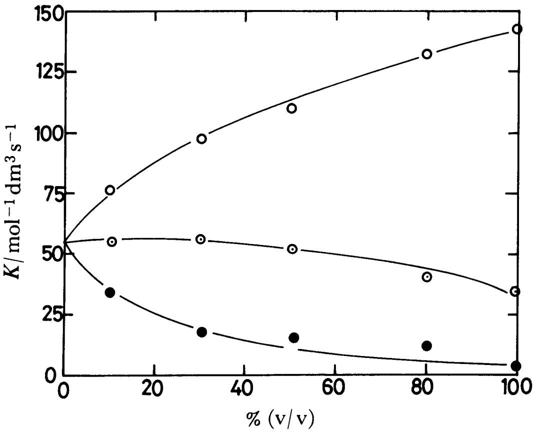


Fig. 3. The effect of solvents on the rate constant of the chlorination reaction: O, dichloromethane; ⊙, acetone; ●, diethyl ether.

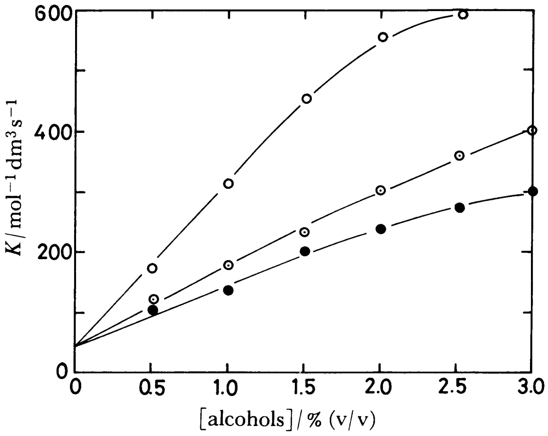
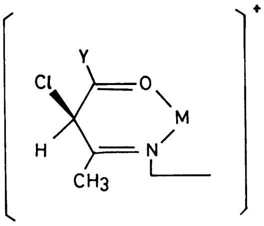


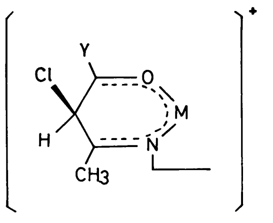
Fig. 4. The effect of alcohols on the rate constant of the chlorination: O, methyl alcohol; ⊙, ethyl alcohol; ●, butyl alcohol.

rate constant. It is reported that molecular chlorine is liberated from CSI by the addition of alcohols.[17] Thus, chlorine liberated by alcohols may accelerate the reaction rate; 6) The rate constants of the chlorination of Cu(L-H, Me, H) and (L-H, Me, H) are $(8.0\pm 1.2)\times 10^2$ and $(1.1\pm 0.2)\times 10^2$/mol^{-1} dm^3 s^{-1}, respectively (Runs 7 and 8).

On the basis of the above results and discussion, the chlorination of M(L-H, Y, Z) can be assumed to proceed *via* an intermediate (A)[9] or (B) in which a π-system is extended through the central metal ion. However, for the free ligand, in which an extended π-system like (B) is impossible, also proceeds the chlorination, and the order of the rate constant is Ni(II)-complex< free ligand<Cu(II)-complex. Therefore, these results indicate that the chlorination of M(L-H, Y, Z) proceeds *via* the intermediate (A) which is consistent with the result for Ni(tfac$_2$en).[9]



(A)



(B)

That is, the electrophilic ring-substitution reaction on the chelate ring of metal complexes does not necessarily support the existence of the benzenoid resonance as shown for the β-diketone metal complexes by Collman *et al.*[5] The results agree with those obtained by the ^{1}H NMR studies.

The copper(II) complex shows an extremely large rate constant as compared with the nickel(II) complex and the free ligand. At present, there is no satisfactory explanation for the behavior of the copper(II) complex. The copper(II) complex may catalyze the reaction presumably *via* the formation of a CSI adduct. Further studies on the effect of the central metal ions will be performed.

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