Oxidation of (7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine)nickel(II) Complexes

Mamoru Hashimoto and Kazunori Sakata*

Department of Chemistry, Faculty of Engineering,
Kyushu Institute of Technology,
Tobata-ku, Kitakyushu 804, Japan

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The oxidation reaction of two isomers of (7,16-diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*]-[1,4,8,11]tetraazacyclotetradecine)nickel(II) diperchlorate and/or dichloride (NiL^1X_2 ($X = ClO_4$, Cl)) in methanol in air under atmospheric pressure leads to the production of (7,16-diethyl-5,6,7,8,9-pentahydrodibenzo-[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) complexes (NiL^2X). Proton and ^{13}C nmr spectra suggest that NiL^2X is formed by partial oxidation from a macrocyclic skeleton of NiL^1X_2. The dehydrogenation of NiL^1X_2 does not occur at symmetric positions such as *d*- and *k*-positions of the macrocyclic skeleton but at unsymmetrical positions such as *d*- and *f*-positions. Treatment of NiL^1X_2 and/or NiL^2X in a methanol solution with an excess of bases in air gives (7,16-diethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) (NiL^3).

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Introduction.

For some time, we have been interested in the coordination chemistry of tetraaza[14]annulene complexes containing benzene rings [1], pyridine rings [2] and pyrazine rings [3]. The dibenzocyclam was prepared from tetraaza[14]-annulene containing benzene rings by hydrogenation [4]. Recently, we have synthesized and isolated two isomers (L^1(a) and L^1(b)) of dibenzocyclams having ethyl groups at 7- and 16-positions of the macrocyclic skeleton [5]. Furthermore, the nickel(II), copper(II) and zinc(II) complexes of isomers L^1(a) and L^1(b) have been prepared and investigated with regard to their spectroscopic properties by us [5].

In the present work, we have synthesized and oxidated NiL^1X_2 ($X = ClO_4$, Cl). Oxidative changes in NiL^1X_2 were attributable to oxidation of the macrocyclic skeleton of the nickel(II) complex and led to NiL^2X and NiL^3. We characterized the spectral properties of NiL^2X by means of visible, infrared and nmr spectroscopy.

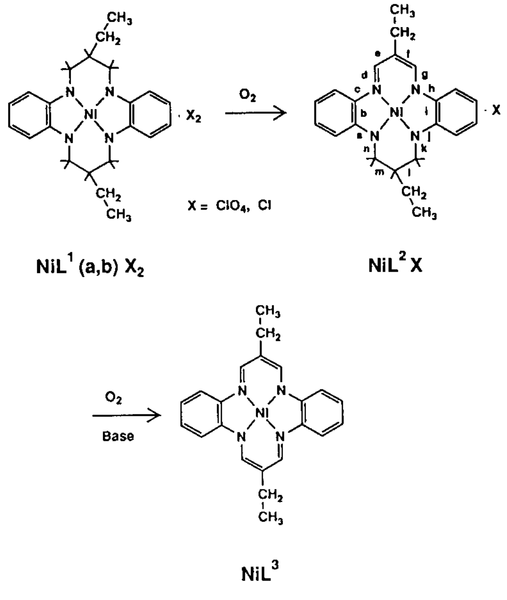
Results and Discussion.

Preparation and Properties of Macrocycles and their Nickel(II) Complexes.

Treatment of the two isomers of 7,16-diethyl-5,6,7,8,9,-14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (L^1(a) and L^1(b)) with nickel(II) chloride hexahydrate gave the corresponding complexes $NiLX_2$ ($L = L^1$(a) or L^1(b); $X = ClO_4$ or Cl) in good yields, as described previously [4a].

The nickel(II) complexes are soluble in polar solvents, and unstable in solution when allowed to stand in contact with air in the atmosphere. The color of a freshly prepared dilute methanol solution of nickel(II) diperchlorate complexes changes from pale yellow to deep green and, further, to reddish orange. This seems to indicate that oxidation of the nickel(II) complexes occurs in 2 days at 30°. The same oxidation reaction also occurs in 4 days at 30° in a methanol solution of nickel(II) dichloride complexes. On the other hand, the nickel(II) complexes are stable in methanol solution while argon was continuously bubbled through it, and were recovered unchanged. These facts show that the nickel(II) complexes are ultimately oxidized by molecular oxygen. The structure of these oxidized nickel(II) complexes is investigated by means of spectroscopy, and become NiL^2X as shown in Scheme 1. Ansell and co-workers synthesized the analogous complexes with another synthetic process, that is, by reaction of 1,3-bis(*o*-aminophenylamino)propane, 3-ethoxy-2-methylacrolein and nickel(II) ions [6]. NiL^1X_2 and/or NiL^2X in methanol are oxidized soon by the addition of excess base, and then NiL^3 are obtained.

Scheme 1



Electronic Spectra.

Ligand-field spectra for $NiL^1(a)(ClO_4)_2$ and $NiL^1(a)Cl_2$ are shown in Figure 1. The ligand-field spectra for two nickel(II) diperchlorate complexes ($NiL^1(a)(ClO_4)_2$ and $NiL^1(b)(ClO_4)_2$) demonstrate only one broad band at about 22000 cm^{-1}, and are similar to each other [5]. Those for the two nickel(II) dichlorides ($NiL^1(a)Cl_2$ and $NiL^1(b)Cl_2$) are similar to each other, and consist of two bands at about 18000 cm^{-1} and below 12500 cm^{-1}. This seems to indicate that $NiL^1(a)(ClO_4)_2$ and $NiL^1(b)(ClO_4)_2$ assume a square-planner configuration, and that $NiL^1(a)Cl_2$ and $NiL^1(b)Cl_2$ assume a distorted octahedral configuration [7,4b].

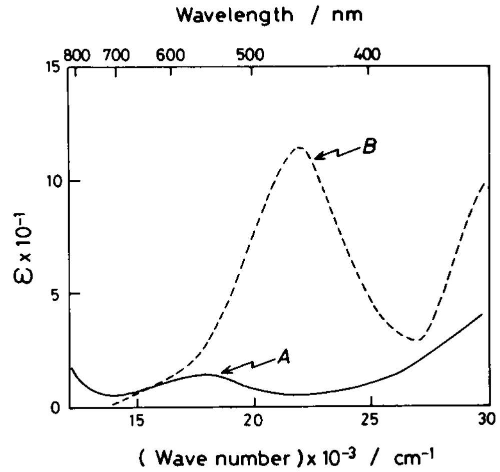


Figure 1. Ligand-field spectra for nickel(II) complexes in acetonitrile at room temperature. *A*, $NiL^1(a)Cl_2$; *B*, $NiL^1(a)(ClO_4)_2$.

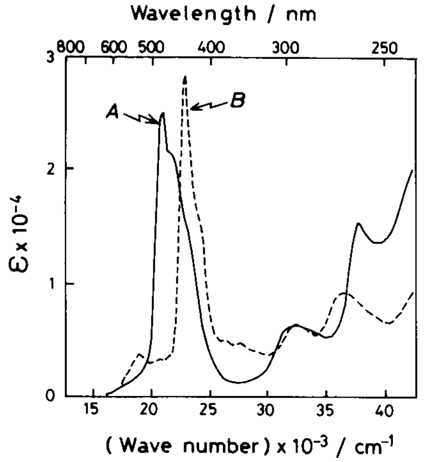


Figure 2. Electronic absorption spectra for nickel(II) complexes in acetonitrile at room temperature. *A*, NiL^2ClO_4; *B*, NiL^3.

The electronic absorption spectrum for NiL^2ClO_4 is shown in Figure 2 together with that of NiL^3. The absorption bands in the 20800 cm^{-1} region are reasonably attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand, because the molar extinction coefficients of the bands ($\sim 10^4$ mol^{-1} cm^{-1} l) are larger than those normally assigned to ligand-field transitions [8]. Further, these bands were observed in the vicinity of the bands of NiL^3 (22700 cm^{-1}) reported previously [1b]. These facts have suggested that the dehydrogenation take place in the macrocyclic skeleton of the nickel(II) complexes and that longer conjugated systems are formed. The ligand-field bands were not assigned for the complexes, because all the ligand-field bands were obscured by the $\pi \rightarrow \pi^*$ and CT bands of high intensity.

Molar Conductances.

The molar conductances for the nickel(II) complexes are summarized in Table I. NiL^2ClO_4 is a 1:1 electrolyte and is four-coordinated in acetonitrile solution [9]. Hence, the perchlorate anion is ionized on solution in the solvent. The conductance values of $NiL^1(a)Cl_2$, $NiL^1(b)Cl_2$ and NiL^2Cl are much smaller in magnitude than those of NiL^2ClO_4. These facts show that chloride anions are not ionized in the solvent. $NiL^1(a)Cl_2$ and $NiL^1(b)Cl_2$ are hexa-coordinated with two chloride anion in the axial site, but NiL^2Cl are penta-coordinated with one chloride anion at the axial site in acetonitrile. This result is consistent with the corresponding electronic spectral behavior.

Table I

Molar Conductances for the Nickel(II) Complexes at 25° [a]

Complex	Λ_M S(cm^2 mol^{-1})	Type of electrolyte [b]	Reference
$NiL^1(a)(ClO_4)_2$	352 [c]	3 (1:2)	5
$NiL^1(b)(ClO_4)_2$	368 [c]	3 (1:2)	5
$NiL^1(a)Cl_2$	32.1	0	
$NiL^1(b)Cl_2$	32.2	0	
NiL^2ClO_4	138.5	2 (1:1)	
NiL^2Cl	37.2	0	

[a] Measured in acetonitrile. For *ca.* 10^{-3} mol dm^{-3} solutions. [b] Assignment of the type of electrolyte present in solution was made on the basis of the conductance data compiled by Geary [9]. [c] For *ca.* 10^{-4} mol dm^{-3} solutions.

Vibrational Spectra.

The vibrational mode at *ca.* 3200 cm^{-1} which is associated with a N-H stretching mode in L^1(a, b) and NiL^1(a, b)X_2 (X = ClO_4, Cl) is not visualized owing to oxidation of the nickel(II) complexes as shown in Figure 3. A strong absorption bands newly observed in the 1464 cm^{-1} range is most sensitive to oxidation reaction of $NiL^1(b)(ClO_4)_2$ among the absorption peaks appearing in the NaCl region, and can be attributed to the stretching mode of C=C and C=N bonds. A strong broad band at around 1100 cm^{-1} was observed for the NiL^2ClO_4 and $NiL^1(ClO_4)_2$

and is attributable to the stretching vibrational mode of the perchlorate ion. The perchlorate group is present not as a coordinated group but as a isolated ion as judged by the vibrational frequency [10]. This result is in fair agreement with that of molar conductances described above. Another peak due to the perchlorate group was observed at about 620 cm^{-1} which is attributed to its bending vibration [10].

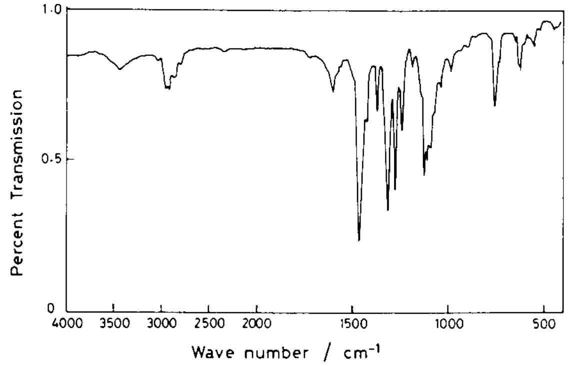


Figure 3. Infrared spectrum for NiL^2ClO_4 at room temperature (potassium bromide disk method).

NMR Spectra.

The ^1H nmr spectral data of NiL^2ClO_4 are compiled in Table II. The methyl protons of metal-free macrocycles L^1(a, b) and those zinc(II) complexes ($ZnL^1(ClO_4)_2$) couple with methylene protons and the methyl proton signals are split into a triplet [4]. The methyl proton signals for NiL^2ClO_4 are observed as a sextet. This peak is analyzed as the overlapping of two triplets (1.06 and 1.20 ppm). The position of methyl proton signals at 1.06 ppm are similar to that of macrocycles L^1 and assigned to originate from ethyl group substituted for methylene of saturated macrocyclic skeleton [5]. On the other hand, the methyl proton signals at 1.20 ppm do not be found in the spectrum for L^1. The signals (2.45 and 7.58 ppm) were found to vanish upon oxidation of $NiL^1(ClO_4)_2$. The pattern of three signals (1.20, 2.45 and 7.58 ppm) is similar to that of NiL^3 and the three signals are attributable to methyl, methylene and methine proton signals, respectively. It can be assumed that there are two kinds of chain such as L^1 containing a saturated chain and L^3 containing a unsaturated chain in the macrocyclic skeleton of the nickel(II) complexes.

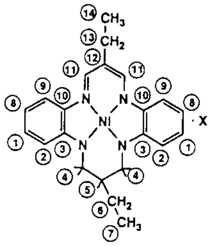


Table II

Proton NMR Data for the Macrocycles and Nickel(II) Complexes [a]

Compound	Aromatic	–NH	N–CH$_2$– N–CH=	–CH–	–CH$_2$	–CH$_3$	Reference
L^1 (a)	6.5-6.9 (m)	4.38 (s)	2.7-3.6 (m)	2.1 (m)	1.48 (m)	1.09 (t)	5
L^1 (b)	6.5-6.9 (m)	4.20 (s)	2.7-3.6 (m)	2.1 (m)	1.47 (m)	1.09 (t)	5
NiL^2ClO_4	6.9-7.6 (m)	5.71 (s)	3.1-3.3 (m)	2.0 (m)	1.42 (m)	1.06 (t, J = 7.6 Hz)	
			7.58 (s)		2.45 (q, J = 7.6 Hz)	1.20 (t, J = 7.6 Hz)	
NiL^3	6.7-7.4 (m)		7.62 (s)		2.42 (q, J = 7.4 Hz)	1.19 (t, J = 7.4 Hz)	1b

[a] Chemical shifts in ppm from internal TMS. Measured in chloroform-d. Multiplicity of a proton signal is given in parentheses after the δ-value; s = singlet; t = triplet; q = quartet; m = multiplet.

Table III

^{13}C NMR Data for the Macrocycles and Nickel(II) Complexes [a]

Compound	C(1) C(8)	C(2) C(9)	C(3) C(10)	C(4) C(11)	C(5) C(12)	C(6) C(13)	C(7) C(14)	solvent	Reference
L^1 (a)	117.57	109.45	137.40	50.93	–	25.66	12.23	HMPT-d_{18}	5
				50.07	38.01	25.15			
L^1 (b)	117.57	109.45	137.40	50.93	37.95	25.66	12.23	HMPT-d_{18}	5
NiL^2ClO_4	124.71	114.42	138.03	56.87	–	23.03	10.74	DMSO-d_6	
	128.31	123.63	147.74	144.66	112.48	24.01	17.83		
NiL^3	123.74	113.85	137.63	147.35	110.20	25.66	17.98	$CDCl_3$	

[a] Chemical shift in ppm from internal TMS.

The ^{13}C nmr data and their assignments for L^1, NiL^2X and NiL^3 are compiled in Table III. ^{13}C nmr can be used in the identification of the nickel(II) complexes. In the ^{13}C nmr spectrum for NiL^2X, there are two kinds of spectral peaks such as the peaks of saturated dibenzocyclam skeleton (5-9) and unsaturated dibenzoannulene skeleton (14-18). Consequently, NiL^1X_2 are dehydrogenated on no symmetric position (*d*- and *k*-positions) but a unsymmetric position (*d*- and *f*-positions) of cyclam skeleton.

EXPERIMENTAL

Unless otherwise noted all materials were reagent grade and were used without further purification.

Conductivity measurements were made on acetonitrile solutions of the complexes kept at 25.0±0.1° with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured with a TOA Electronics LTD, CM-20E. FAB mass spectra (in a matrix of neat glycerin) for NiL^1(a, b)Cl, NiL^2ClO_4 and NiL^2Cl and the EI mass spectra (at 70 eV) for NiL^3 were obtained on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. Argon was used as the fast-atom beam. Infrared spectra in the range of the 400-4000 cm^{-1} were carried out with a Hitachi 260-30 spectrophotometer at room temperature by the potassium bromide disk method. Ultraviolet and visible spectra covering the 12500-50000 cm^{-1} region were taken on a Shimadzu UV 200S double beam spectrophotometer at room temperature. Proton and ^{13}C nmr measurements were recorded on a JEOL JNM-FX 60 spectrometer. The nmr spectra were run in chloroform-d and dimethyl sulfoxide-d_6, and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard.

Preparation of Nickel(II) Complexes.

(7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,-8,11]tetraazacyclotetradecine)nickel(II) Diperchlorate (NiL^1(a)($ClO_4)_2$ and NiL^1(b)($ClO_4)_2$).

The synthetic procedures for NiL^1(a)($ClO_4)_2$ and NiL^1(b)($ClO_4)_2$ have been reported previously [5].

(7,16-Diethyl-5,6,7,8,9,14,15,16,17,18-decahydrodibenzo[*b,i*][1,4,-8,11]tetraazacyclotetradecine)nickel(II) Dichloride (NiL^1(a)Cl_2 and NiL^1(b)Cl_2).

(A) A mixture of L^1(a) (0.18 g), nickel(II) chloride hexahydrate (0.15 g) and methanol (20 ml) was heated at 60° for 4 hours with stirring under argon atmosphere. Upon cooling the reaction mixture with an ice water bath for 12 hours, the crystalline solid was recovered by filtration and washed several times with cold methanol to give 0.16 g (65%) of violet plates (NiL^1(a)Cl_2), mp 223-227° dec; ir: ν N-H 3215, ν C=C 1600, 1494, 1454, δ C-H 752 cm^{-1}; uv (acetonitrile): λ max 558 (ϵ = 14), 259 (ϵ = 5300), 227 nm (ϵ = 9870); ms: m/z (relative intensity) 413 (11.1), 412 (23.4), 411 (49.2), 410 (56.6), 409 (100), 408 (26.3), 407 (16.7).

Anal. Calcd. for $C_{22}H_{32}N_4NiCl_2$: C, 54.81; H, 6.69; N, 11.62. Found: C, 54.87; H, 6.66; N, 11.60.

(B) L^1(b) (0.18 g), nickel(II) chloride hexahydrate (0.15 g) and methanol (20 ml) were reacted as described above for 4 hours to yield 0.18 g (73%) of violet plates (NiL^1(b)Cl_2), mp 234-239° dec; ir: ν N-H 3215, ν C=C 1600, 1492, 1454, δ C-H 760 cm^{-1}; uv (acetonitrile): λ max 557 (ϵ = 18), 259 (ϵ = 5330), 227 nm (ϵ = 9700); ms: m/z (relative intensity) 412 (9.89), 411 (17.8), 410 (40.0), 409 (45.1), 408 (100), 407 (26.1), 406 (19.6).

Anal. Calcd. for $C_{22}H_{32}N_4NiCl_2$: C, 54.81; H, 6.69; N, 11.62. Found: C, 55.20; H, 6.66; N, 11.57.

Oxidation of NiL^1X_2.

(7,16-Diethyl-5,6,7,8,9-pentahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Perchlorate (NiL^2ClO_4).

Air was bubbled into the methanol (400 ml) solution of suspending NiL^1(b)($ClO_4)_2$ (0.200 g) at 30° for 2 days with stirring. The reaction mixture was evaporated to dryness. The chloroform solution (100 ml) of the residue was washed with water, dried over anhydrous sodium sulfate, and distilled away *in vacuo*. The product was recrystallized from methanol/water/perchloric acid (70%) to give 0.082 g (50%) of red needles (NiL^2ClO_4), mp 226-229° dec; ir: ν C=C 1600, 1464, ν Cl-O 1120-1090, δ C-H 752, δ Cl-O 622 cm^{-1}; ms: m/z (relative intensity) 409 (10.4), 408 (16.1), 407 (44.2), 406 (33.1), 405 (100), 404 (9.8).

Anal. Calcd. for $C_{22}H_{27}N_4NiClO_4$: C, 52.26; H, 5.38; N, 11.08. Found: C, 52.22; H, 5.36; N, 10.70.

Chloro(7,16-diethyl-5,6,7,8,9-pentahydrodibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecinato)nickel(II) (NiL^2Cl).

A methanol (400 ml) solution of NiL^1Cl (0.135 g) was treated for 4 days, following the above procedure. The solid was recrystallized from methanol/water/hydrochloric acid to give 0.061 g (50%) of red needles (NiL^2Cl), mp 230-235° dec; ir: ν C=C 1600, 1462, δ C-H 752 cm^{-1}; ms: m/z (relative intensity) 410 (16.9), 409 (27.4), 408 (29.5), 407 (66.1), 406 (46.9), 405 (100), 404 (10.3).

Anal. Calcd. for $C_{22}H_{27}N_4NiCl$: C, 59.83; H, 6.16; N, 12.69. Found: C, 59.47; H, 6.12; N, 12.62.

7,16-Diethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)-nickel(II) (NiL^3).

A mixture of NiL^1(b)Cl_2 (0.112 g), sodium hydroxide (0.050 g) and methanol (250 ml) was heated at 40° for 7 hours with stirring. Upon cooling the reaction mixture with an ice water bath, the crystalline solid was recovered by filtration and washed several times with methanol (10 ml) to give 0.070 g (80%) of reddish violet crystals (NiL^3), mp 299-301° dec; ir: ν C=N 1609, ν C=C 1596, 1462, δ C-H 736 cm^{-1}; ms: m/z (relative intensity) 385 (88.0), 386 (23.0), 387 (36.6), 388 (10.4), 400 (100), 401 (27.9), 402 (42.2), 403 (12.4).

Anal. Calcd. for $C_{22}H_{22}N_4Ni$: C, 65.87; H, 5.53; N, 13.97. Found: C, 65.77; H, 5.57; N, 13.90.

Oxidation of NiL^2ClO_4.

7,16-Diethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)-nickel(II) (NiL^3).

A mixture of NiL^2ClO_4 (0.10 g), sodium hydroxide (0.10 g) and methanol (200 ml) was heated at 40° for 4 hours with stirring. Upon cooling the reaction mixture with an ice water bath, the crystalline solid was recovered by filtration and washed several times with methanol (10 ml) to give 0.055 g (70%) of reddish violet crystals (NiL^3).

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