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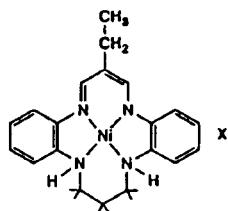
The eight nickel(II) complexes with 16-ethyl-5,6,7,8,9,14-hexahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine and a counter anion have been synthesized and their spectroscopic properties were studied. The δ N-H values of NiLCl and NiLBr are observed in a more downfield range than those of NiLPF₆, NiLBF₄ and NiLClO₄ in acetonitrile and nitromethane solutions. The plot of δ N-H against molar conductance is found to be approximately linear. The N-H stretching modes of NiLBF₄, NiLPF₆ and NiLClO₄ shift to lower frequency and those of NiLCl, NiLBr and NiLi shift to higher frequency upon metal-coordination.

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Introduction.

Much attention has been paid to the chemistry of tetraazamacrocyclic complexes [1]. Dibenzo[14]annulene ligand has a planar array of four nitrogens in a highly conjugated π -electron system analogous to porphyrin and phthalocyanine. All these ligands form complexes with a variety of metals, possessing a dianion. Cyclam and 1,4,8,11-tetramethylcyclam which act as neutral ligands give ionic metal complexes. Recently, we have synthesized dibenzocyclams and their metal complexes [2]. Furthermore, we have oxidized the nickel(II) complexes with air to (7,16-diethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) complexes and/or (7,16-diethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecinato)nickel(II) complex [3].

In the present work, we have synthesized (16-ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecinato)nickel(II) complexes (NiLX) with eight types of counter anions X. We characterized the spectral properties of NiLX by means of visible, infrared, nmr and mass spectroscopy in order to explore the counter anion effect.



NiLX

Preparation of Macrocycle and its Nickel(II) Complexes.

The treatment of 1,3-bis(2-aminophenylamino)propane and 3-ethoxy-2-ethylacrolein led to the corresponding macrocycle HL in satisfactory yield by non-metal template reaction. The reaction of the nickel(II) salt with HL gave the corresponding nickel(II) complex in good yield.

The analytical data of the macrocycle and the nickel(II) complexes are listed in Table I. Elemental analyses of these crystalline samples were in fair agreement with compounds of these expected compositions.

Table I
Analytical Data for Macrocycle and its Nickel(II) Complexes

Compound	Empirical Formula	Elemental Analyses		
		Calcd./Found (%)		
		C	H	N
HL	C ₂₀ H ₂₄ N ₄	74.97 75.12	7.55 7.67	17.48 17.39
NiLCl·H ₂ O	C ₂₀ H ₂₃ N ₄ NiCl·H ₂ O	55.66 55.59	5.84 5.71	12.98 12.90
NiLBr	C ₂₀ H ₂₃ N ₄ NiBr	52.45 52.69	5.06 4.89	12.23 12.23
NiLi	C ₂₀ H ₂₃ N ₄ NiI	47.57 47.39	4.59 4.76	11.09 11.10
NiLNO ₃	C ₂₀ H ₂₃ N ₄ NiNO ₃	54.58 54.84	5.28 5.19	15.91 15.70
NiLNCS	C ₂₀ H ₂₃ N ₄ NiNCS	57.82 57.62	5.31 5.26	16.06 15.89
NiLClO ₄	C ₂₀ H ₂₃ N ₄ NiClO ₄	50.30 50.44	4.85 4.86	11.73 11.58
NiLBF ₄	C ₂₀ H ₂₃ N ₄ NiBF ₄	51.67 51.45	4.99 4.92	12.05 11.98
NiLPF ₆	C ₂₀ H ₂₃ N ₄ NiPF ₆	45.92 45.93	4.43 4.41	10.71 10.68

Electronic Spectra.

The electronic absorption spectrum for NiLCl in acetonitrile is shown in Figure 1 together with that of macrocycle HL. The absorption bands observed above 20900 cm⁻¹ region are reasonably attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand since the molar extinction coefficients of the bands ($\sim 10^4$ mol⁻¹cm⁻¹) are much larger than those commonly assigned to ligand-field transitions [3,4]. Those bands for the eight nickel(II) complexes (NiLX, X = Cl, Br, I, NO₃, NCS, ClO₄, BF₄, PF₆) are similar to

each other. The ligand-field bands were not assigned for the present complexes, because all the ligand-field bands were obscured by intense $\pi \rightarrow \pi^*$ and CT transition bands. The absorption bands due to $\pi \rightarrow \pi^*$ and CT bands are not influenced by any anion.

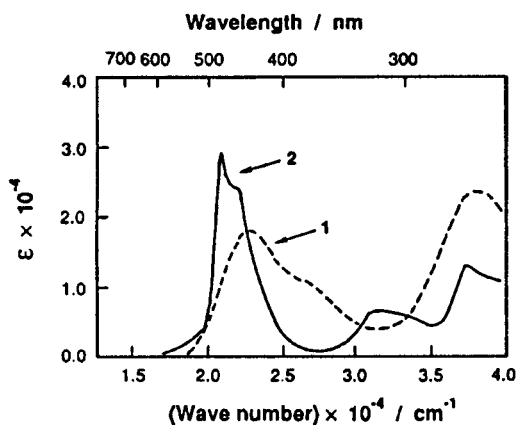


Figure 1. Electronic absorption spectra of macrocyclic ligand and its nickel(II) complex in acetonitrile at room temperature (1, HL, 2, NiLCl).

Molar Conductances.

The molar conductances for the nickel(II) complexes are compiled in Table II. NiLPF₆, NiLBF₄, NiLClO₄ and NiLNCS are 1:1 electrolytes and are tetra-coordinated in

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

Complex	$\Lambda_M S(\text{cm}^2\text{mol}^{-1})$		Type of electrolyte [b]
	Acetonitrile	Nitromethane	
NiLCl	24.2	16.1	0
NiLBr	49.3	22.3	0
NiLi	92.4	45.5	0-2
NiLNO ₃	81.8	38.4	0-2
NiLNCS	121.7	68.5	2 (1:1)
NiLClO ₄	139.7	86.6	2 (1:1)
NiLBF ₄	115.8	70.3	2 (1:1)
NiLPF ₆	123.8	71.1	2 (1:1)

[a] For ca. 10^{-3} mol dm⁻³ solutions. [b] Assignment of the type of electrolyte presented in solutions was made on the basis of the conductance data listed by Geary [5].

acetonitrile and nitromethane solutions [5]. Therefore, it is noted that the PF₆, BF₄, ClO₄ and NCS anions of the nickel(II) complexes ionize in the solvent. The conductance values of NiLCl and NiLBr are much smaller in magnitude than those of a 1:1 electrolyte. This fact shows that chloride and bromide anions are not ionized in the solvents. Both NiLCl and NiLBr are penta-coordinated complexes by taking up a chloride and/or a bromide anion in the axial site.

NMR Spectra.

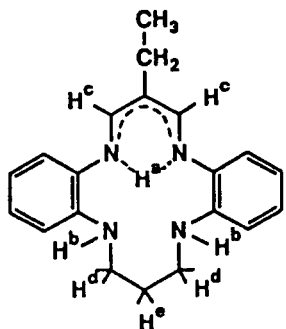
The proton nmr data of HL and NiLX are collected in Table III. The H^c-methine proton of metal-free macrocy-

Table III
Proton NMR Data for the Macrocyclic Ligand and its Nickel(II) Complexes [a]

Compound	Arom	NH ^{a,b}	CH ^c	CH ₂ ^d	CH ₂ ^e	-CH ₂ -	-CH ₃
HL	6.6-7.2 (m)	12.37 (t, J = 5.1 Hz) 4.70 (s)	7.83 (d, J = 5.1 Hz)	3.43 (t, J = 5.1 Hz)	1.8-2.3 (m)	2.36 (q, J = 7.3 Hz)	1.18 (t, J = 7.3 Hz)
NiLPF ₆	6.8-7.6 (m)	4.8 (s)	7.57 (s)	3.37 (m)	2.2 (m)	2.46 (q, J = 7.2 Hz)	1.20 (t, J = 7.2 Hz)
NiLBF ₄	6.7-7.7 (m)	5.34 (s)	7.55 (s)	3.36 (m)	2.3 (m)	2.43 (q, J = 7.4 Hz)	1.19 (t, J = 7.4 Hz)
NiLClO ₄	6.9-7.7 (m)	5.6 (s)	7.58 (s)	3.39 (m)	2.2 (m)	2.46 (q, J = 7.6 Hz)	1.20 (t, J = 7.6 Hz)
NiLNO ₃	6.8-7.6 (m)	6.3 (s)	7.58 (s)	3.35 (m)	2.3 (m)	2.44 (q, J = 7.4 Hz)	1.19 (t, J = 7.4 Hz)
NiLNCS	6.8-7.5 (m)	6.57 (s)	7.57 (s)	3.36 (m)	2.2 (m)	2.44 (q, J = 7.5 Hz)	1.20 (t, J = 7.5 Hz)
NiLi	6.7-7.6 (m)	6.8 (s)	7.57 (s)	3.41 (m)	2.2 (m)	2.44 (q, J = 7.4 Hz)	1.19 (t, J = 7.4 Hz)
NiLBr	6.8-7.6 (m)	7.4 (s)	7.57 (s)	3.38 (m)	2.2 (m)	2.43 (q, J = 7.5 Hz)	1.18 (t, J = 7.5 Hz)
NiLCl	6.8-7.6 (m)	6.9 (s)	7.58 (s)	3.53 (m)	2.2 (m)	2.42 (q, J = 7.4 Hz)	1.17 (t, J = 7.4 Hz)

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

cle couples with the H^a-amine proton, and the H^c-signal is split into a doublet, while the H^a-signal is split into a triplet owing to coupling with both H^c-methine protons. The H^a-signal is found to disappear upon nickel-coordina-



tion, whereupon H^c-signal appears as a singlet and indicates slightly up-field shifts. The H^b-amine signals are observed as broad peaks, and indicate downfield shifts upon formation of the nickel(II) complexes. Figure 2 and

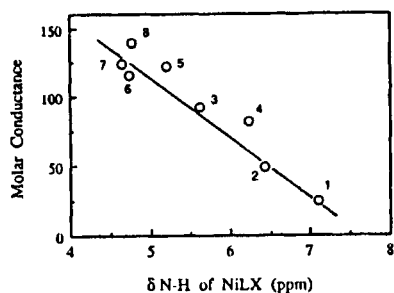


Figure 2. The correlation between δ N-H values and molar conductances of nickel(II) complexes in acetonitrile solutions (1, NiLCl, 2, NiLBr, 3, NiLi, 4, NiLNO₃, 5, NiLNCS, 6, NiLBF₄, 7, NiLPF₆, 8, NiLClO₄).

3 illustrate the plot for δ N-H value of the nickel(II) complexes vs. molar conductance in acetonitrile and nitromethane solutions. Inspection of Figure 2 shows that the

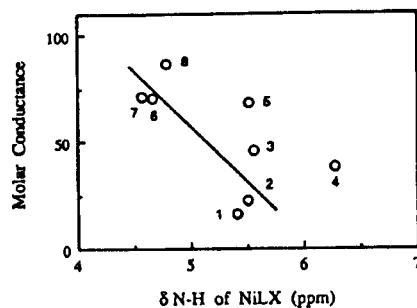


Figure 3. The correlation between δ N-H values and molar conductances of nickel(II) complexes in nitromethane solutions. (1, NiLCl, 2, NiLBr, 3, NiLi, 4, NiLNO₃, 5, NiLNCS, 6, NiLBF₄, 7, NiLPF₆, 8, NiLClO₄).

plot of δ N-H value against molar conductance is found to be nearly linear. The δ N-H value of NiLBr which is penta-coordinated with a bromide anion in the axial site, is observed in lower field (1.7-1.8 ppm) than those of NiLPF₆, NiLBF₄ and NiLClO₄ with ionized anions (PF₆⁻, BF₄⁻ and/or ClO₄⁻) in acetonitrile solutions. The plot of δ N-H value against molar conductance is also found to be approximately linear in nitromethane solutions. This is due to electron-withdrawing effect of the anion group. The δ N-H values in seven solvents are summarized in Table IV, and the plot for δ N-H value of HL vs. δ N-H value of NiLX is shown in Figure 4. The amine peaks of NiLX are observed in the wide range of the 0.8-2.6 ppm in each solvent. The peaks of NiLPF₆, NiLBF₄ and NiLClO₄ exhibit down-field shift in chloroform-d, acetone-d₆, *N,N*-dimethylformamide-d₇ and dimethyl sulfoxide-d₆ solutions, and reveal an up-field shift in nitromethane-d₃, acetonitrile-d₃ and pyridine-d₅ solutions (Figure 4). The peaks of NiLCl, NiLBr and NiLi are observed at lower field (0.8-2.6 ppm) than those of NiLPF₆, NiLBF₄ and NiLClO₄ without a pyridine-d₅ solution. This is ascribed to the electron-withdrawing effect of chloride, bromide and/or iodide atoms of the counter anion.

Table IV

δ N-H Values of the Macrocyclic and its Nickel(II) Complexes [a]

Compound	Solvent						
	CDCl ₃	(CD ₃) ₂ CO	CD ₃ CN	DMSO-d ₆	Py-d ₅	CD ₃ NO ₂	DMF-d ₇
HL	4.70	5.23	5.03	5.70	5.97	4.89	5.66
NiLPF ₆	4.8	5.79	4.64	6.11	5.76	4.57	6.37
NiLBF ₄	5.34	5.54	4.74	6.11	5.5	4.66	6.38
NiLClO ₄	5.6	5.6	4.77	6.12	5.4	4.78	6.37
NiLNCS	6.57	6.4	5.20	6.14	5.3	5.52	6.42
NiLNO ₃	7.3	[b]	6.23	6.18	5.23	6.27	6.66
NiLi	6.8	[b]	5.62	6.13	5.08	5.55	6.48
NiLBr	7.4	[b]	6.44	6.34	5.02	5.50	7.1
NiLCl	7.3	7.1	7.1	6.93	5.17	5.40	7.7

[a] Chemical shifts in ppm from TMS. [b] The peak can not be observed because of insolubility.

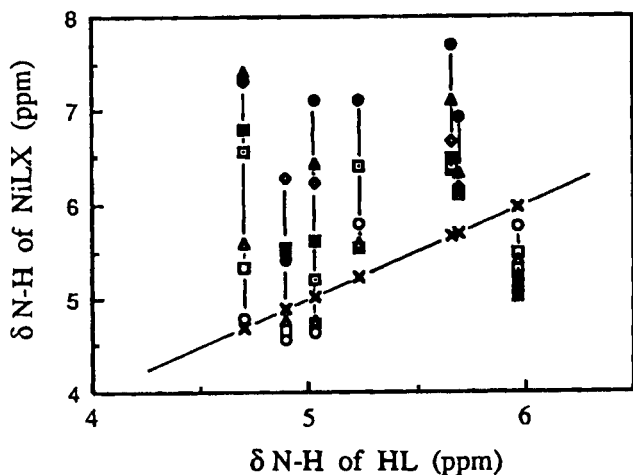


Figure 4. The correlation between δ N-H value of HL and that of NiLX in various solutions (x, HL, ●, NiLCl, ▲, NiLBr, ■, NiLI, ◆, NiLNO₃, ◻, NiLNCS, ◻, NiLBF₄, ◻, NiLPF₆, ▲, NiLClO₄).

Vibrational Spectra.

A strong absorption band observed in the range of the 3200–3500 cm^{-1} is attributable to a N-H stretching mode. These bands of NiLPF₆, NiLBF₄ and NiLClO₄ are shifted to lower frequency upon nickel-coordination. It is considered that the drop in electron density of nitrogen atoms by the coordination results in a lowering of the N-H frequency. On the other hand, the N-H bands of NiLCl, NiLBr and NiLI shift to higher frequency upon nickel-coordination. This shows that Cl, Br and/or I anions cause a much larger shift (130–240 cm^{-1}) to higher frequency than PF₆, BF₄ and/or ClO₄ because of the former anion coordination to nickel atom.

A strong broad band around 1100 cm^{-1} , 1050 cm^{-1} and/or 840 cm^{-1} was observed for NiLClO₄, NiLBF₄ and/or NiLPF₆ and attributed to the stretching vibrational mode of perchlorate, fluoroborate and hexafluorophosphate, respectively [6].

Mass Spectra.

The FAB mass spectra of nickel(II) complexes NiLX, obtained in a glycerin matrix, show a cluster of ions at m/z 377 corresponding to $[M-X]^+$. Besides the major fragment at m/z 377 ($[M-X]^+$), the masses of NiLCl, NiLBr and NiLI establish a cluster of ions at m/z 789, 834 or 882, respectively. The peak at m/z 789 is corresponding to $[\text{NiL-Cl-NiL}]^+$, and those at m/z 834 and 882 correspond to $\{[\text{NiL-X-NiL}]+H\}^+$ ($X = \text{Br, I}$). This fact seems to indicate that chloride, bromide and/or iodide anions are coordinated to nickel in the solid state.

EXPERIMENTAL

Unless otherwise noted all materials were reagent grade and

were used without further purification. Ultraviolet and visible spectra covering the 12500–50000 cm^{-1} region were taken on a Shimadzu UV 200S double beam spectrophotometer at room temperature. Conductivity measurements were made in acetonitrile and nitromethane solutions of the complexes thermostated at $25.0 \pm 0.1^\circ$ with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured with a TOA Electronics LTD, CM-20E instrument. Proton nmr measurements were recorded using a JEOL JNM-FX 60 spectrometer. The nmr spectra were run in chloroform-*d*, acetone-*d*₆, acetonitrile-*d*₃, nitromethane-*d*₃, dimethyl sulfoxide-*d*₆, *N,N*-dimethylformamide-*d*₇ and pyridine-*d*₅ and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard. Infrared spectra in the range of the 400–4000 cm^{-1} were carried out with a JEOL JIR-5500 FT-IR spectrophotometer and a Hitachi 260-30 spectrophotometer at room temperature in a Nujol mull and/or a potassium bromide disk. FAB mass spectra (in a matrix of neat glycerin) for nickel(II) complexes and the EI mass spectra (at 70 eV) for macrocycle HL were obtained on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer. Argon was employed as the fast-atom beam. Melting points were determined with a Yanaco MP-S3 micro melting point apparatus (hot-plate type).

Preparation of Macrocycle and Nickel(II) Complexes.

16-Ethyl-5,6,7,8,9,14-hexahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (HL).

A mixture of 1,3-bis(2-aminophenylamino)propane [7] (10.0 g), 3-ethoxy-2-ethylacrolein [8] (5.7 ml) and toluene (500 ml) was heated under reflux for 4 hours while nitrogen gas was continuously bubbled through it. After the solvent was evaporated off *in vacuo*, methanol was added to the oily residue. A precipitate was separated by filtration, washed with methanol and recrystallized from methanol to give 5.5 g (44%) of reddish yellow needles, mp 156.0–157.3°; ir: ν N-H 3350, ν C=N 1633, ν C=C 1595, 1531, 1500, C-H 737 cm^{-1} ; ms: m/z (relative intensity) 320 (100) 321 (25.1) 322 (3.7); uv (acetonitrile): λ max 440 (17700), 376 sh (10300), 264 (23200).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Chloride (NiLCl).

A mixture of HL (160 mg), nickel(II) chloride hexahydrate (143 mg) and methanol (30 ml) was stirred for 1 hour at room temperature. Water (30 ml) and ammonium chloride (2.0 g) was added to the reaction mixture. A precipitate was isolated by filtration and washed with water to give 128 mg (62%) of deep red needles, mp 155° dec; ir: ν N-H 3386 ν C=N 1601, ν C=C 1470, C-H 750 cm^{-1} ; ms: m/z (relative intensity) 377 (100), 378 (29.7), 379 (46.0), 380 (13.8), 789 (4.1), 790 (2.4), 791 (5.2), 792 (2.7), 793 (2.9); uv (acetonitrile): λ max 479 (28700), 458 sh (23900), 309 (6590), 267 (13000), 236 (21600).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Bromide (NiLBr).

This was prepared from HL (160 mg), nickel(II) acetate tetrahydrate (150 mg), methanol (50 ml), water (30 ml) and ammonium bromide (2.0 g), following the above procedure, and was recovered by filtration to obtain 218 mg (95%) of deep red needles, mp 247° dec; ir: ν N-H 3415, 3344, ν C=N 1601, ν C=C 1471, C-H 756 cm^{-1} ; ms: m/z (relative intensity) 377 (100), 378 (31.8), 379 (43.6), 380 (14.1), 834 (2.0), 835 (0.9), 836 (3.5), 837 (2.1), 838 (3.0), 839 (1.7), 840 (1.1); uv (acetonitrile):

trile): λ max 479 (24900), 458 sh (21100), 305 (7640), 266 (17600).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Iodide (NiLI).

This complex was prepared from **HL** (160 mg), nickel(II) acetate tetrahydrate (150 mg), methanol (50 ml), water (30 ml) and ammonium iodide (2.0 g), following the above procedure, and was isolated by filtration to yield 241 mg (95%) of dark red needles, mp 220° dec; ir: ν N-H 3450, 3377, ν C=N 1597, ν C=C 1470, C-H 756 cm^{-1} ; ms: *m/z* (relative intensity) 377 (100), 378 (36.2), 379 (48.9), 380 (16.3), 882 (1.1), 884 (1.0), 886 (1.4); uv (acetonitrile): λ max 479 (25000), 457 sh (23200), 305 (7380), 266 sh (16300), 244 (25500).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Isothiocyanate (NiLNCs).

A mixture of **HL** (160 mg), nickel(II) acetate tetrahydrate (150 mg) and methanol (50 ml) was stirred for 40 minutes at room temperature. Water (30 ml) and ammonium thiocyanate (2.0 g) was added to the reaction mixture. A precipitate was separated by filtration and washed with water to give 213 mg (98%) of dark red microcrystals, mp 230° dec; ir: ν N-H 3062, ν NCS 2040, ν C=N 1601, ν C=C 1464, C-H 746 cm^{-1} ; ms: *m/z* (relative intensity) 377 (100), 378 (31.2), 379 (44.4), 380 (13.6); uv (acetonitrile): λ max 479 (24800), 458 sh (21000), 308 (7710), 266 (14600), 234 (21600).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Nitrate (NiLNO₃).

This was prepared from **HL** (160 mg), nickel(II) acetate tetrahydrate (150 mg), methanol (50 ml), water (30 ml) and ammonium nitrate (2.0 g), following the above procedure, and there was obtained by filtration 195 mg (89%) of dark red needles, mp 208° dec; ir: ν N-H 3064, ν C=N 1603, ν C=C 1470, C-H 756 cm^{-1} ; ms: *m/z* (relative intensity) 377 (100), 378 (79.1), 379 (66.2), 380 (22.2); uv (acetonitrile): λ max 479 (28000), 457 sh (22200), 307 (7460), 266 (17600), 231 sh (23900).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Perchlorate (NiLClO₄).

A mixture of **HL** (160 mg), nickel(II) perchlorate hexahydrate (220 mg) and methanol (30 ml) was stirred for 2 hours at room temperature. Water (30 ml) and ammonium perchlorate (2.0 g) was added to the reaction mixture. A precipitate was isolated by filtration and washed with water to give 151 mg (67%) of dull red needles, mp 155° dec; ir: ν N-H 3213, 3167, ν C=N 1603, ν C=C 1471, ν Cl-O 1110, 1084, C-H 756, Cl-O 625 cm^{-1} ; ms: *m/z* (relative intensity) 377 (100), 378 (31.7), 379 (44.7); uv (acetonitrile): λ max 479 (32200), 458 sh (25700), 307 (7300), 266 (14000), 236 (20400).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraaza-

cyclotetradecinato)nickel(II) Fluoroborate (NiLBF₆).

This complex was prepared from **HL** (160 mg), nickel(II) acetate tetrahydrate (150 mg), methanol (50 ml), water (30 ml) and ammonium fluoroborate (2.0 g), following the above procedure, and there was obtained by filtration 216 mg (93%) of dull red needles, mp 237° dec, ir: ν N-H 3230, ν C=N 1601, ν C=C 1466, ν B-F 1084, 1041, C-H 756 cm^{-1} ; ms: *m/z* (relative intensity) 377 (100), 378 (30.9), 379 (40.5), 380 (13.7); uv (acetonitrile): λ max 479 (25700), 457 sh (20700), 307 (7350), 266 (17600).

(16-Ethyl-5,6,7,8-tetrahydro-9*H*-dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)nickel(II) Hexafluorophosphate (NiLPF₆).

This was prepared from **HL** (160 mg), nickel(II) acetate tetrahydrate (150 mg), methanol (50 ml), water (30 ml) and ammonium hexafluorophosphate (2.0 g), following the above procedure, and there was obtained by filtration 240 mg (92%) of dull red prisms, mp 242° dec; ir: ν N-H 3261, ν C=N 1601, ν C=C 1464, ν P-F 843, 822, C-H 748, P-F 555 cm^{-1} ; ms: *m/z* (relative intensity) 377 (100), 378 (29.4), 379 (46.0), 380 (17.2); uv (acetonitrile): λ max 479 (28900), 456 sh (23300), 306 (7410), 266 (18200), 233 (24100).

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