Formation of an *N*,*N*-Bidentate Chelate, Bis[4-(4-methyl-2-pyridylazo)resorcinol]nickel(II) Perchlorate, in Dioxane

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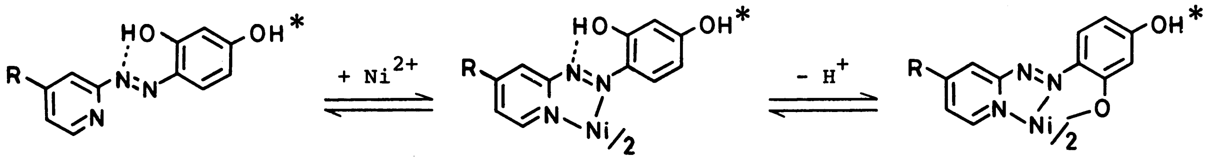
The formation of a new *N*,*N*-bidentate complex of nickel(II) perchlorate with an *N*,*N*,*O*-terdentate ligand, 4-(4-methyl-2-pyridylazo)resorcinol (4-MePAR), was first detected in dioxane spectrophotometrically. The stability of the *N*,*N*-bidentate species in dioxane is strongly affected by the presence of a proton acceptor such as water, ethanol, imidazole, and Cl^-, which promote the coordination of the *ortho* phenolic oxygen in the ligand to form the *N*,*N*,*O*-terdentate complex. The new complex was isolated from dioxane solution and identified to be an *N*,*N*-bidentate complex salt, $[Ni(4\text{-mepar})_2](ClO_4)_2$, having two counter ions, ClO_4^-. A distorted-planar configuration of the complex was suggested on the basis of IR, X-ray photoelectron spectroscopic, and magnetic measurements.

o-(Pyridylazo)phenol compounds coordinate to metal ions to form *N*,*N*,*O*-terdentate complexes in aqueous media.[1,2] Kinetic studies on the reactions of 4-(2-pyridylazo)resorcinol (PAR)[3] and 1-(2-pyridylazo)-2-naphthol (*β*-PAN)[4] with nickel(II) ion in aqueous solution suggested the following reaction mechanism involving the formation of an *N*,*N*-bidentate complex (II) as an intermediate. However, the intermediate complex II presumed in the scheme 1 has not been detected so far.[5]

In the present study, the formation of the *N*,*N*-bidentate complex II of nickel(II) perchlorate with 4-(4-methyl-2-pyridylazo)resorcinol (4-MePAR) was first detected spectrophotometrically in an aprotic solvent, 1,4-dioxane. The stability of the *N*,*N*-bidentate complex strongly depends on the solvent basicity and/or the presence of a proton acceptor.

The intermediate bidentate complex II was first isolated as a perchlorate from dioxane solution and identified.



(1)

I
LHH*[†]
PAR: R=H; 4-MePAR: R=Me

II
$[Ni(LHH^*)_2]^{2+}$

III
$[Ni(LH^*)_2]^0$

Experimental

Materials. Deionized water was distilled. Reagent grade materials were used unless otherwise specified.

Nickel(II) perchlorate monohydrate was obtained by heating recrystallized hexahydrate at 90±5 °C for 5 h *in vacuo* and kept in a desiccator over P_2O_5. The nickel(II) content in the monohydrate was determined titrimetrically with EDTA. The concentrations of the solutions were calculated from the weighed amount.

The ligands, 4-MePAR,[6] 4-(2-pyridylazo)phenol (*p*-PAP),[7] and 5-dimethylamino-2-(2-pyridylazo)phenol (DAPAP),[8] were synthesized as described in the literature. The concentrations of the solutions were calculated from the weighed amount.

In order to remove peroxides, dioxane (Wako) was passed through a column of basic alumina, dried with sodium metal, and distilled under argon immediately before use.

Syntheses of the Nickel(II) Complexes. 1) *N,N,O-Terdentate Complex*: $[Ni(LH^*)_2]^0$. The complex was prepared by mixing an aqueous solution of nickel(II) chloride (3.1 mmol) with that of 4-MePAR (3.9 mmol). The reddish brown complex was identified to be $Ni(C_{12}H_{10}N_3O_2)_2$ by elemental analysis.

2) *N,N-Bidentate Complex*: $[Ni(LHH^*)_2](ClO_4)_2$. 4-MePAR (200 mg, 0.87 mmol) was dissolved in dioxane (*ca.* 200 cm^3) under argon atmosphere. To the solution $Ni(ClO_4)_2 \cdot H_2O$ (100 mg, 0.36 mmol) suspended in dioxane (*ca.* 100 cm^3) was slowly added. The mixture was stirred for several hours and allowed to stand overnight in the dark under argon atmosphere. The yellowish red precipitate was filtered, washed with dioxane, and dried for 2 d *in vacuo* over P_2O_5. Yield *ca.* 40%. Found: C, 40.01; H, 3.19; N, 11.49; Cl, 8.83%.[9] Calcd for $Ni(C_{12}H_{11}N_3O_2)_2(ClO_4)_2$: C, 40.26; H, 3.10; N, 11.74; Cl, 9.90%.

3) *Other Nickel(II) Complexes.* The 1:2 complex of nickel(II) with *p*-PAP, $[Ni(pap)_2]^0 \cdot H_2O$, was synthesized as reported in the literature.[7] The *N*,*N*-bidentate nickel(II) complex of DAPAP was prepared and purified by the same method as that for the synthesis of $[Ni(LHH^*)_2](ClO_4)_2$. The isolated complex was identified to be $Ni(C_{13}H_{14}N_4O)_2(ClO_4)_2 \cdot 2H_2O$ by elemental analysis.

Measurements. Since most of the reagents used in the study were moisture-sensitive, all measurements were performed under dry argon atmosphere. All sample solutions were prepared in a glove bag filled with dry argon.

Visible absorption spectra were measured at 25.0±0.3 °C with a Hitachi EPS-3T recording spectrophotometer.

The IR spectra were measured with a JASCO IR-G infrared spectrophotometer in the region 4000—400 cm^{-1} with use of

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[†] The ligand is abbreviated as LHH*, where H and H* denote the protons of the *ortho* and the *para* hydroxyl group, respectively.

the KBr pellet technique. The KBr disk was carefully prepared under dry argon atmosphere. The influence of the moisture during the measurements was negligibly small.

X-Ray photoelectron spectra were obtained for powdered samples using an electron spectrometer Model VG ESCA 3. Mg $K\alpha$ (1253.6 eV) X-ray radiation was used as the excitation source. The measurements were conducted at room temperature under a vacuum of *ca.* 10^{-6} Pa.

The magnetic susceptibilities of the nickel(II)-4-MePAR complexes were measured at room temperature using Gouy method. Diamagnetic corrections for the ligands were calculated from Pascal's constants; -32.0×10^{-6} c.g.s emu mol^{-1} was used as the correction for perchlorate ion.[10]

The ^1H NMR data for the dioxane solution of the new complex were not obtained owing to very low solubility.

The pH* of the aqueous dioxane solution was measured at 25 °C with a Hitachi-Horiba pH-meter Model F-7ss. The values of pC_H ($=-\log C_H$) were calculated by the following relationship between pH-meter readings (pH*) and the values of $\log U_H$: $pC_H = pH^* + \log U_H$.[11]

Results and Discussion

Spectral Changes in the Complex Formations of Nickel(II) Perchlorate with 4-MePAR. Figure 1(a) shows the spectral changes in the complex formation of nickel(II) perchlorate with 4-MePAR in 10%(v/v) dioxane-water at pH* 4.2. Upon addition of nickel(II) perchlorate to the solution of 4-MePAR, the absorption around 380 nm due to 4-MePAR decreased with the increase of a new absorption at 511 nm; a well-defined isosbestic point was observed at 465 nm, which indicates the presence of a simple equilibrium. Molar ratio method indicates the formation of a 1:2 nickel(II) complex. The feature of the final spectrum of the complex (Curve 5) is essentially the same as the absorption spectrum of the *N,N,O*-terdentate 1:2 complex of PAR in 10%(v/v) dioxane-water,[12] namely, the final spectrum is ascribed to the *N,N,O*-terdentate complex, $[Ni(LH^*)_2]^0$.

In neat dioxane, different spectral changes were observed. Figure 1(b) shows the spectral changes observed upon addition of nickel(II) perchlorate to the dioxane solution of 4-MePAR. The absorption around 380 nm due to the free ligand decreased with the increase of new absorption around 420 and 480 nm with a single isosbestic point at 399 nm (Curves 1→3) in the region of the low concentrations of nickel(II) perchlorate ($[Ni(II)]_t/[4\text{-MePAR}]_t \leqq 0.3$). With further increase in the concentration of nickel(II) perchlorate, a new absorption peak appeared (λ_{max}=430 and 470 nm (sh)) with another set of isosbestic points at 400 and 471 nm (Curves 4→6). These spectral changes suggest the existence of two successive equilibria.

Molar ratio method indicated the formation of a 1:3 and a 1:2 nickel(II) complex in the first and the second step of the reaction, respectively.[13] The final spectrum of the 1:2 nickel(II) complex (Curve 6) clearly differs from the spectrum characteristic of the *N,N,O*-terdentate 1:2 complex (Curve 5 in Fig. 1(a)).

Electronic Spectra of the Isolated Nickel(II) Complexes in Dioxane. Figure 2 shows the electronic spectra in dioxane of the free ligand 4-MePAR, the isolated new yellowish red complex, $[Ni(C_{12}H_{11}N_3O_2)_2](ClO_4)_2$, and the terdentate complex, $[Ni(LH^*)_2]^0$.

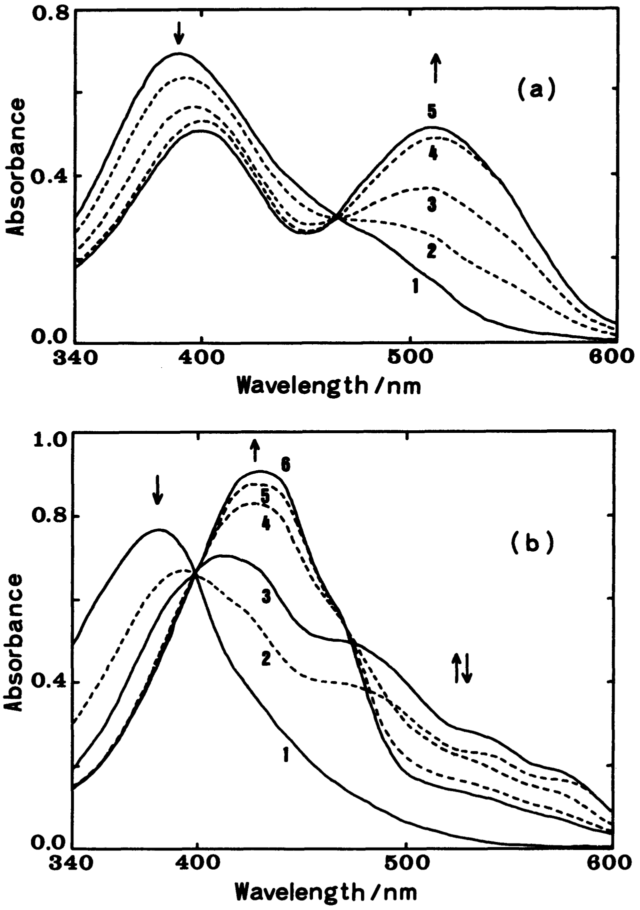


Fig. 1. (a) Spectral change upon addition of nickel(II) perchlorate to the 10% (v/v) dioxane-water solution of 4-MePAR at pH*=4.2, I=0.1 mol dm^{-3} ($NaClO_4$), and 25 °C.
$[4\text{-MePAR}]_t = 3.67\times10^{-5}$ mol dm^{-3} ($[\ ]_t$ denotes the total concentration). $[Ni(II)]_t$=0.00 (1), 0.48 (2), 0.95 (3), 3.17 (4), and 15.8×10^{-5} mol dm^{-3} (5).
(b) Spectral change upon addition of nickel(II) perchlorate to the dioxane solution of 4-MePAR at 25 °C.
$[4\text{-MePAR}]_t = 3.65\times10^{-5}$ mol dm^{-3}. $[Ni(II)]_t$=0.00 (1), 0.41 (2), 1.03 (3), 1.64 (4), 1.97 (5), and 19.7 $\times10^{-5}$ mol dm^{-3} (6).

The absorption spectrum of the free ligand has a single peak at 381 nm ($\varepsilon_{max}=2.10\times10^4$ mol^{-1} dm^3 cm^{-1}) (Curve 1). The spectra of the complexes show the large bathochromic shifts compared with the spectrum of the free ligand. The spectrum of the new complex with a single peak at 426 nm ($\varepsilon_{max}=3.90\times10^4$ mol^{-1} dm^3 cm^{-1}) and a shoulder around 470 nm ($\varepsilon_{sh}=3\times10^4$ mol^{-1} dm^3 cm^{-1}) (Curve 2) essentially coincides with that of the dioxane solution prepared by mixing a large excess of nickel(II) perchlorate with 4-MePAR (Curve 6 in Fig. 1(b)). The spectrum of the bis-terdentate complex, $[Ni(LH^*)_2]^0$, has two absorption bands at 400 (ε_{max}= 3.2×10^4) and 542 nm ($\varepsilon_{max}=3.2\times10^4$ mol^{-1} dm^3 cm^{-1}) in dioxane (Curve 3).

The feature of the absorption spectrum with two bands is characteristic of the coordination of the *ortho* phenolic oxygen in the ligand. The spectrum of the new complex is quite different from that of the *N,N,O*-

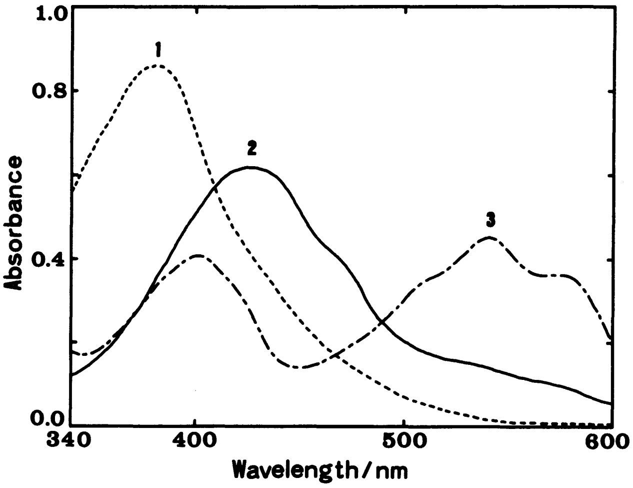


Fig. 2. Electronic spectra of the free ligand 4-MePAR and its nickel(II) complexes at 25 °C in neat dioxane. (1) 4-MePAR: $[\mathrm{LHH^*}]_t = 4.09 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$; (2) the new complex: $[\mathrm{Ni(C_{12}H_{11}N_3O_2)_2(ClO_4)_2}]_t = 1.57 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$; (3) the *N,N,O*-terdentate complex: $[\mathrm{Ni(LH^*)_2^0}]_t = 1.3 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$.

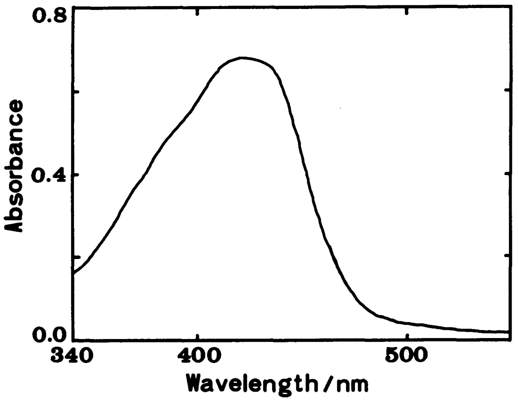
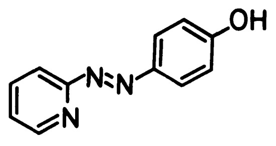


Fig. 3. Electronic spectrum of the *N,N*-bidentate chelate between nickel(II) perchlorate and *p*-PAP at 25 °C in dioxane.
$[\mathrm{Ni(II)}]_t = 5.25 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$, $[p\text{-PAP}]_t = 3.63 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$.

terdentate complex, $[\mathrm{Ni(LH^*)_2}]^0$. Furthermore, the spectrum of the new complex is similar to that of the *N,N*-bidentate 1:2 nickel(II) complex of *p*-PAP with no coordinating *o*-hydroxyl group (Fig. 3).



p-PAP

These observations indicate that the new complex has an *N,N*-bidentate structure with uncoordinated *ortho* phenolic oxygen. This conclusion is also supported by the elemental analysis; the isolated new complex is $[\mathrm{Ni(LHH^*)_2}](\mathrm{ClO_4})_2$ having two perchlorate ions as counter ions.

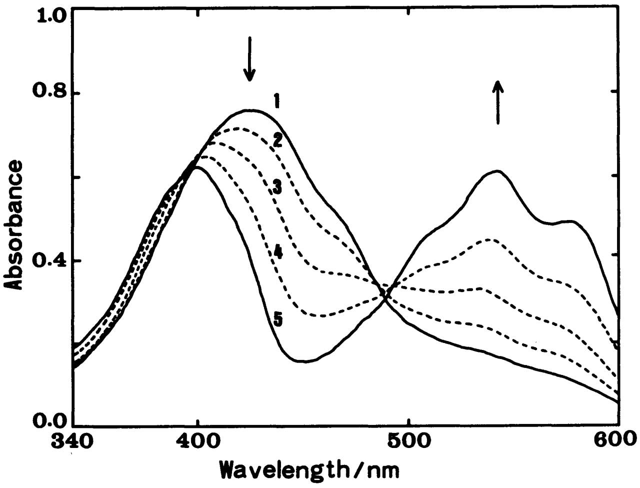
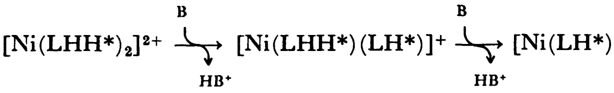


Fig. 4. Spectral change observed on addition of imidazole to the $1.52 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$ dioxane solution of the new complex at 25 °C.
$[\mathrm{Imidazole}]_t = 0.00$ (1), 0.60 (2), 1.19 (3), 2.09 (4), and $7.46 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$.

Reactions of Brønsted Bases with the New Bidentate Complex. The formation of the *N,N*-bidentate complex in dioxane was seriously influenced by the presence of a Brønsted base as a proton acceptor which would promote the release of the *ortho* phenolic proton and the subsequent formation of the *N,N,O*-terdentate complex.

Upon addition of a nitrogen base, imidazole, to the dioxane solution of the new complex, the yellow solution turned pink. Figure 4 shows the spectral change upon addition of imidazole to the solution of the new complex; two-step reactions were demonstrated by two sets of isosbestic points at 403 and 485, and 392 and 493 nm. The final spectrum essentially coincides with the spectrum of the dioxane solution of the *N,N,O*-terdentate complex, $[\mathrm{Ni(LH^*)_2}]^0$, isolated from aqueous solution. This indicates that the observed spectral change results from the coordination of the *ortho* phenolic oxygen of the ligand; imidazole acts as a proton acceptor and not as a ligand.

The stoichiometry of the two-step reaction between the bidentate complex and imidazole, B, was found to be 1:1 for the first step and 1:2 for the overall reaction by molar ratio method. The feature of the spectral change is explained by the following reaction scheme,



$$[\mathrm{Ni(LHH^*)_2}]^{2+} \xrightarrow[\mathrm{HB^+}]{\mathrm{B}} [\mathrm{Ni(LHH^*)(LH^*)}]^{+} \xrightarrow[\mathrm{HB^+}]{\mathrm{B}} [\mathrm{Ni(LH^*)_2}]^{0}. \qquad (2)$$

yellow orange pink

The same spectral change was observed upon addition of water or ethanol to the dioxane solution of the new complex. The addition of tetrabutylammonium chloride to the dioxane solution of the new complex also gave the similar spectral change. This result suggests a role as a proton acceptor of chloride ion.[14]

Liberation of ortho *Protons from the New Bidentate Complex in Aqueous Media.* In the solution pre-

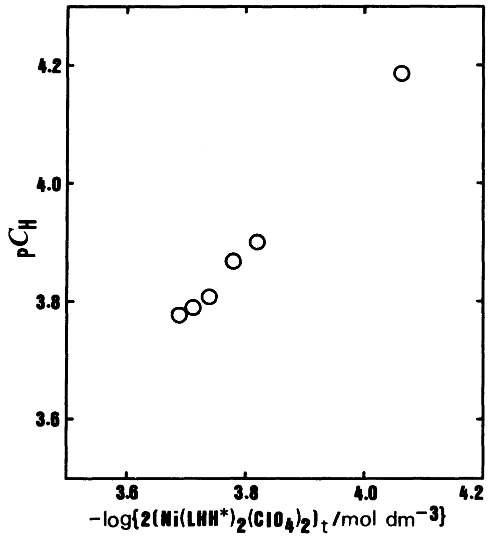
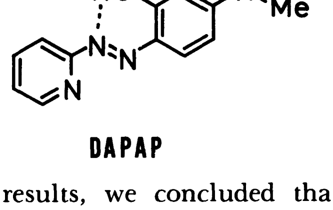


Fig. 5. Plot of pC_H *vs.* $-\log\{2[Ni(LHH^*)_2(ClO_4)_2]_t\}$ in 10%(v/v) dioxane-water at 25 °C.

pared by dissolving the new complex in 10%(v/v) dioxane-water the characteristic absorption peak at 426 nm of the new complex was not observed, instead, the two absorption bands around 400 and 511 nm were observed, which were ascribed to the *N,N,O*-terdentate complex, $[Ni(LH^*)_2]^0$. The pH* values of the solutions were lowered in accordance with the amount of the dissolved new complex. The plot of the values of pC_H against $-\log\{2[Ni(LHH^*)_2(ClO_4)_2]_t\}$ demonstrates the liberation of two protons from the new complex (Fig. 5). The liberation of protons should be owed to the *ortho* protons of the *N,N*-bidentate complex: $[Ni(LHH^*)_2]^{2+}+2H_2O \rightarrow [Ni(LH^*)_2]^0+2H_3O^+$, since the *para* protons of the terdentate complex, $[Ni(LH^*)_2]^0$, could not be dissociated under the experimental conditions.[15] In addition, the spectral and pH measurements in the similar experiments with the nickel(II) complex, isolated from dioxane, of DAPAP having no *p*-hydroxyl group gave the same results as those for the new bidentate complex, $[Ni(LHH^*)_2](ClO_4)_2$.



DAPAP

From these results, we concluded that the new yellowish red complex is the *N,N*-bidentate intermediate complex II proposed in the Scheme 1.

Possible Configuration of the Isolated New Complex. The IR spectrum of the new complex perchlorate, $[Ni(LHH^*)_2](ClO_4)_2$, shows a single strong broad band at 1060—1150 cm^{-1}, which corresponds to the $\nu_{Cl\text{-}O}$ of the free perchlorate ion, ClO_4^-. This indicates that the perchlorate anions do not coordinate to the central nickel(II) atom.[16]

The binding energy of Ni(II)($2p_{3/2}$) bonded to the same ligands under different geometries increases in general in the order of a square-planar (*ca.* 853—854 eV), a tetrahedral (*ca.* 853—854 eV), and an octahedral configuration (*ca.* 855 eV).[17]

TABLE 1. CORE ELECTRON BINDING ENERGIES AND MAGNETIC MOMENTS OF THE FREE LIGANDS AND THEIR NICKEL(II) COMPLEXES

Species	Binding energy[a]/eV			μ_{eff}[b]/BM
	N(1s)	O(1s)	Ni($2p_{3/2}$)	
LHH*	395[c]	528		
	398.3[c]	531.3		
$[Ni(LHH^*)_2](ClO_4)_2$	400.0[c]	—[d]	853	3.04
$[Ni(LH^*)_2]^0$	400.3[c]	528	856	3.08
		532.1		
p-PAP	399.2[c]	531.2		
$[Ni(pap)_2]^0\cdot H_2O$	399.6[c]	514.7	853	
		520.4		
$[NiCl_2(phen)_2]^0\cdot 4H_2O$[e]	398.3		854.1	
Bpy[f]	398.6			
$[NiCl_2(bpy)_2]^0$,[e]	399.1		854.9	

a) All raw binding energies were corrected to hydrocarbon C(1s) value of 285.0 eV.[20] b) Measured at 290 K. c) Ref. 19. d) Unable to measure due to the strong O(1s) signal of the perchlorate ion. e) Ref. 17. f) Ref. 18.

The X-ray photoelectron spectral data of the free ligands and their nickel(II) complexes are summarized in Table 1 together with the data of magnetic moments. The increase in the binding energy of N(1s) of the ligand on the formation of the complexes, $[Ni(LH^*)_2]^0$,[19] $[Ni(pap)_2]^0\cdot H_2O$,[19] and $[NiCl_2(bpy)_2]^0$,[17] is due to the coordination of the nitrogen atoms to the nickel(II) atom.[20] A positive chemical shift in the N(1s) binding energy observed in the new complex suggests the coordination of the nitrogen atoms to nickel(II) in the complex, $[Ni(LHH^*)_2](ClO_4)_2$. The Ni(II)($2p_{3/2}$) binding energy of the new complex formulated as $[Ni(LHH^*)_2](ClO_4)_2$ is in good agreement with that of a four-coordinated complex, $[Ni(pap)_2]^0\cdot H_2O$, and is obviously lower than that of the typical octahedral complexes, $[Ni(LH^*)_2]^0$, $[NiCl_2(phen)_2]^0\cdot 4H_2O$,[17] and $[NiCl_2(bpy)_2]^0$.[17]

These X-ray photoelectron spectral data strongly suggest the four-coordinated *N,N*-bidentate structure for the complex, $[Ni(LHH^*)_2](ClO_4)_2$.

The magnetic moments, μ_{eff}, of four-coordinated nickel(II) complexes in general depend on its spin-state and ligand field symmetry.[21] The magnetic moment of $[Ni(LHH^*)_2](ClO_4)_2$ was found to be 3.04 BM at 290 K. This value suggests that the new complex, $[Ni(LHH^*)_2](ClO_4)_2$, has a distorted-planar structure.

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14) The formation of the new complex was not observed also in the reactions of nickel(II) chloride, acetate, and nitrate with 4-MePAR in neat dioxane. These results indicate the role of the counter-ion, Cl^-, CH_3COO^-, and NO_3^-, as a proton acceptor in dioxane. However, perchlorate ion, ClO_4^-, does not act as a proton acceptor in dioxane.

15) The pK_{a1} and pK_{a2} values in 10%(v/v) dioxane–water for the dissociation of the two *p*-hydroxyl protons in the bis-terdentate complex, $[Ni(LH^*)_2]^0 \xrightleftharpoons{pK_{a1}} [Ni(LH^*)L]^- + H^+ \xrightleftharpoons{pK_{a2}} [NiL_2]^{2-} + 2H^+$, were determined by pH titration to be 5.82 and 7.09, respectively. See, H. Shimoda, N. Yoshida, and M. Fujimoto, presented at the 1980 Winter Meeting in Hokkaido of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, Sapporo, February 1, 1980, Abstracts, p. 38.

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