

Steric Crowding Effect of 1,3-Diketonates on the Structures and the Solution Behaviors of Nickel(II) Mixed-Ligand Complexes

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Seven nickel(II) mixed-ligand complexes were synthesized: Ni(dike)(diam)X, where dike is a 1,3-diketonate such as 3,5-heptanedionate (dedk) or 2,6-dimethyl-3,5-heptanedionate (dmhd), diam is an *N*-alkylated ethylenediamine such as *N,N,N',N'*-tetramethylethylenediamine (tmen) or 1,2-dipiperidinoethane (dipe), and X is BPh₄[−] or NO₃[−]. The crystal structures were analyzed: each nitrate complex has a six-coordinated octahedral structure with a bidentate-coordinated nitrate, and each tetraphenylborate complex has a four-coordinated square-planar structure. The ligand field strength of [Ni(dike)(diam)]BPh₄ in the solid state increases in the order: [Ni(dmhd)(dipe)]BPh₄ < [Ni(dedk)(dipe)]BPh₄ < [Ni(dmhd)(tmen)]BPh₄ = [Ni(dedk)(tmen)]BPh₄. In solution, the change of the color depending on the donor/acceptor ability of the solvent, i.e., solvatochromism was observed. When dimethyl sulfoxide was added to a solution of [Ni(dike)(diam)]BPh₄ in inert 1,2-dichloroethane, the adduct formation constants are in the order: [Ni(dmhd)(dipe)]BPh₄ < [Ni(dedk)(dipe)]BPh₄ ≪ [Ni(dmhd)(tmen)]BPh₄ = [Ni(dedk)(tmen)]BPh₄, reflecting the difference in steric hindrance of the ligands rather than the difference in ligand field strength. The steric crowding effect of 1,3-diketonates was observed in the solid state and solution when bulky dipe is used as diamine.

Some 3d transition-metal complexes have a color due to a d–d transition which depends on the coordination structure. For example, nickel(II) can form four-, five-, and six-coordinated complexes and exhibit a variety of colors. We have synthesized a series of mixed-ligand nickel(II) complexes with 1,3-diketonate (dike) and *N*-alkylated ethylenediamine (diam) ligands, Ni(dike)(diam)X where X is a mono-anion.^{1–4} We adopted the mixed-ligand system of the sterically hindered diam and the slim dike to obtain a stable complex and to control the environment of the nickel(II) center finely. This type of complex shows remarkable solvatochromism due to an equilibrium among the octahedral (Oh) and square-planar (Sp) structures. When X is non-coordinating tetraphenylborate ion, the structure remains square-planar in inert solvent such as 1,2-dichloroethane. On the other hand, in solvent with strong donor ability, such as dimethyl sulfoxide, two solvent molecules coordinate to nickel(II) and the Sp ⇌ Oh equilibrium shifts to the right. In solvent with medium donor ability such as acetone, two species coexist. In our research, Gutmann's donor number (DN) is used for the parameter of the donor ability of the solvent, and acceptor number (AN) is used for that of the acceptor ability of the solvent.⁵ Quantitative approaches have been also performed in this mixed-ligand nickel(II) system by determining the equilibrium constant,^{3,6,7} which reflects the degree of the interaction between the complex and the solvent molecules.

Solvatochromic behavior of Ni(dike)(diam)X is affected by the steric crowding around the nickel(II) center and the ligand field stabilization energy. Larger steric hindrance and/or stronger ligand field strength of the complex more stabilizes the square-planar structure. The effect of steric hindrance of

diam has been studied in previous work.^{2,4} So far, the steric effect of dike has been considered rather small since substituent groups on dike protrude away from the nickel(II) center. Even the steric hindrance of the bulky *tert*-butyl substituents on dipm (=dipivaloylmethanate) is obscured by its strong electron-releasing property. In order to know the “pure” steric effect of dike on properties of the mixed-ligand nickel(II) complex, we used two 1,3-diketonate ligands here: 3,5-heptanedionate (dedk) and 2,6-dimethyl-3,5-heptanedionate (dmhd) shown in Figure 1. Since the Hammett's σ_m values of ethyl- and isopropyl groups are the same ($\sigma_m = -0.08$),⁸ these ligands can be considered to have the same electron-releasing property, and the steric crowding of dmhd is larger than that of dedk. Hence properties of the complexes having the same conditions of the nickel(II) center except for dike should reflect the steric hindrance of dike. For diamine ligands, at first, most common *N,N,N',N'*-tetramethylethylenediamine (tmen, Figure 1) was

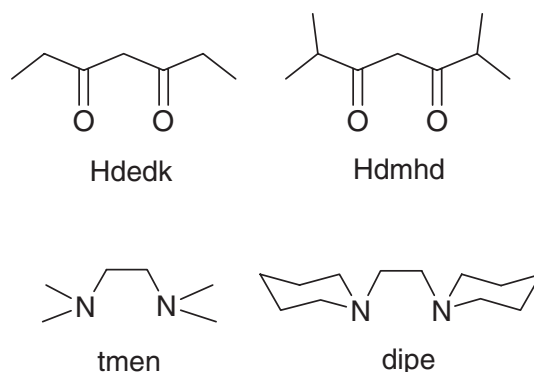


Figure 1. Structures of ligands used in this study.

used, which allows us to easily compare with many analogous complexes $\text{Ni}(\text{dike})(\text{tmen})\text{X}$.¹ Bulky and rigid 1,2-dipiperidinoethane (dipe, Figure 1) was then adopted because the dipe ligand is known to make the solvatochromism of the complex more remarkable than that of tmen complex due to the steric effect of the bulky piperidine rings.²

In the view of these molecular designs, seven solvatochromic complexes are newly obtained: $[\text{Ni}(\text{dedk})(\text{tmen})(\text{NO}_3)]$ (**1a**), $[\text{Ni}(\text{dmhd})(\text{tmen})(\text{NO}_3)]$ (**2a**), $[\text{Ni}(\text{dedk})(\text{dipe})(\text{NO}_3)]$ (**3a**), $[\text{Ni}(\text{dedk})(\text{tmen})]\text{BPh}_4$ (**1b**), $[\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4$ (**2b**), $[\text{Ni}(\text{dedk})(\text{dipe})]\text{BPh}_4$ (**3b**), and $[\text{Ni}(\text{dmhd})(\text{dipe})]\text{BPh}_4$ (**4b**). The crystal structures of all complexes except for **2b** have been determined by single-crystal X-ray analysis. The properties in solution of the complexes were investigated by UV-vis spectroscopy. For the tetraphenylborate complexes **1b–4b**, the equilibrium constants between the square-planar and adduct species have been determined by the spectral changes associated with the addition of a strong donor solvent molecule. Especially, five-coordinated species have been observed as equilibrium mixtures in the case of dipe complexes **3b** and **4b**. These results are discussed from the viewpoint of the steric crowding effects of the dike ligand.

Results and Discussion

Preparation of Mixed-Ligand Complexes. From a stoichiometric mixture of components in an ethanol solution (this mixture is denoted “ethanol solution [A]”), the nitrate complexes are obtained. Since the nitrate complexes are very soluble in ethanol, 1,2-dichloroethane, and also diethyl ether, it seems that concentration of the solution with cooling is better to obtain crystals. In an attempt to synthesize $[\text{Ni}(\text{dmhd})(\text{dipe})(\text{NO}_3)]$, formation of this complex in ethanol was confirmed by the UV-vis spectrum showing two bands (ν_1 and ν_2 from longer wavelength) with different intensities ($\nu_1 < \nu_2$), which is characteristic for the octahedral structure of $3d^8$ electron metal with bidentate nitrate anion.^{2,3,9} However, it could not be obtained on concentration of the solution; instead, the bis-dmhd complex $[\text{Ni}(\text{dmhd})_2(\text{dipe})]$ was precipitated as powder. Elemental analysis data of **3a** did not agree with the calculated values because of contamination by a colorless impurity which could not be removed by recrystallization. Therefore the data of **3a** were used for rough comparison. Fortunately, a single crystal of **3a** was found in the first precipitate from the synthetic solution.

Tetraphenylborate complexes precipitated together with NaNO_3 after the addition of NaBPh_4 to the “ethanol solution [A]”. $[\text{Ni}(\text{dike})(\text{diam})]\text{BPh}_4$ could be separated from NaNO_3 by dissolving in 1,2-dichloroethane. In previous reports, anion exchange was performed in 1,2-dichloroethane dissolving the nitrate complex. Tetraphenylborate complexes are usually insoluble to ethanol, so the method in this report is also useful when the nitrate complex cannot be obtained as powder, such as the dedk–dipe complex. The crystal of $[\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4$ (**2b**) contained solvent molecules and gradually degraded due to loss of the solvent molecules even at 173 K, preventing X-ray analysis.

Properties of Complexes in Solid State. Analytical data are shown in the experimental section. Complexes **1a**, **2a**, and **3a** are paramagnetic. The solid-state reflectance spectrum of

Table 1. Absorption Spectra of the Nitrate Complexes in Solid State and in Various Solvents^{a)} ($\lambda_{\text{max}}/\text{nm}$, $\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in Parentheses, Concn: $8 \times 10^{-3} \text{ mol dm}^{-3}$)

Complex	Solid DCE	NM	dmsO
$[\text{Ni}(\text{acac})(\text{tmen})(\text{NO}_3)]^{\text{b)}$	1034 1045 (10.1)	1040 (8.5)	1059 (8.0)
	605 614 (19.3)	615 (17.5)	634 (6.3)
		482 (6.5)	
1a	1036 1041 (11.3)	1038 (10.1)	1056 (9.1)
	617 613 (22.3)	615 (21.1)	635 (7.4)
		488 (11.9)	
2a	1034 1038 (16.1)	1034 (9.6)	1052 (9.9)
	612 611 (31.1)	613 (20.0)	631 (7.5)
		487 (10.3)	
$[\text{Ni}(\text{acac})(\text{dipe})(\text{NO}_3)]^{\text{c)}$	1020 1081 (9.1)	1070 (9.6)	1103 (7.3)
	620 628 (19.0)	630 (20.1)	656 (6.0)
		491 (6.75)	
3a	1066 1063	1050	1192
	621 626	624	661
		500 (sh ^{d)})	

a) Donor number and acceptor number of the solvent: DCE, 0 and 17; NM, 2.7 and 21; dmsO, 30 and 19. b) Taken from Ref. 1. c) Taken from Ref. 2. d) sh: shoulder.

each complex shows two bands with different intensities ($\nu_1 < \nu_2$), indicating the octahedral structure with bidentate nitrate anion.^{2,3,9} Comparison of the peak position (λ_{max}) of ν_1 (Table 1) indicates that the ligand field strength of the nitrate complexes ordered as follows:

$$[\text{Ni}(\text{dedk})(\text{dipe})(\text{NO}_3)] \text{ (**3a**)} < [\text{Ni}(\text{dedk})(\text{tmen})(\text{NO}_3)] \text{ (**1a**)} \\ = [\text{Ni}(\text{dmhd})(\text{tmen})(\text{NO}_3)] \text{ (**2a**)} \quad (1)$$

Since the difference between [**1a**, **2a**] and **3a** arises from the diamine ligands (the ligand field strength: tmen > dipe), no steric crowding effect of the dike ligands is observed in the solid state of the nitrate complexes. On the other hand, complexes **1b–4b** are diamagnetic and have one strong band around 490–520 nm in the solid-state reflectance spectra, hence they have a square-planar structure.⁹ Comparison of the λ_{max} values (Table 2) shows that the order of the ligand field strengths of the tetraphenylborate complexes in solid state is the following:

$$[\text{Ni}(\text{dmhd})(\text{dipe})]\text{BPh}_4 \text{ (**4b**)} < [\text{Ni}(\text{dedk})(\text{dipe})]\text{BPh}_4 \text{ (**3b**)} \\ < [\text{Ni}(\text{dedk})(\text{tmen})]\text{BPh}_4 \text{ (**1b**)} \\ = [\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4 \text{ (**2b**)} \quad (2)$$

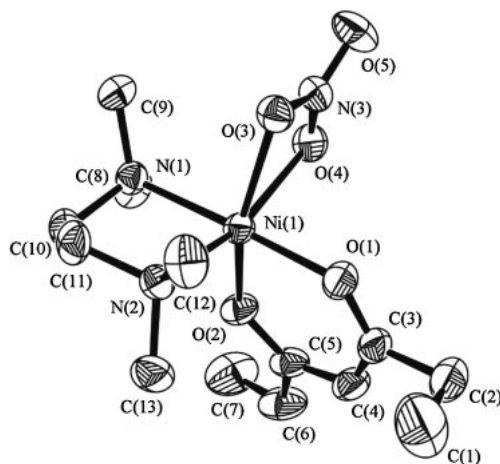
The difference between [**1b**, **2b**] and **3b** is due to the diamine ligands as observed in the nitrate complexes. For tmen complexes **1b** and **2b**, the same λ_{max} values imply no steric crowding effect of the dike ligands. For dipe complexes **3b** and **4b**, the differences in λ_{max} by 14 nm and in the color were observed. The steric repulsion between dipe and dmhd ligands might be larger than that between dipe and dedk.

In the IR spectra, there are weak but important bands due to the coordination mode of NO_3^- in the region of 1700–1800 cm^{-1} , where one band due to the free NO_3^- ion appears. This band splits into two on coordination with a small splitting ($\Delta_{\text{NO}_3} = 20\text{--}25 \text{ cm}^{-1}$) for a monodentate or a

Table 2. Absorption Spectra of the Tetraphenylborate Complexes in Solid State and in Various Solvents^{a)} ($\lambda_{\text{max}}/\text{nm}$, $\epsilon_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ in Parentheses, Conc: $8 \times 10^{-3} \text{mol dm}^{-3}$)

Complex	Solid	DCE	ACN	ACO	dmsO
[Ni(acac)(tmen)]BF ₄ ^{b)}	491 ^{c)}	488 (150.0)	594 (9.5) 993 (9.2)	475 (23.2) 617 (6.3) 1048 (6.4)	633 (6.13) 1055 (8.3)
1b	490	489 (154)	592 (10.4) 997 (9.9)	491 (46.9) 624 (sh) 1050 (7.5)	635 (6.8) 1055 (9.1)
2b	493	489 (158)	597 (17.6) 992 (11.9)	490 (45.1) 610 (sh) 1045 (10.6)	630 (8.8) 1057 (9.6)
[Ni(acac)(dipe)]BPh ₄ ^{b)}	—	496 (89)	622 (4.2) 1026 (3.3)	496 (22.6) 647 (6.9) 1025 (3.2)	661 (4.05) >1100
3b	505	499 (199)	490 (sh) ^{c)} 612 (10.9) 1016 (8.4)	499 (67.3) 659 (9.9) 1040 (5.9)	658 (5.7) 1098 (6.6)
4b	519	499 (203)	490 (sh) ^{c)} 615 (11.3) 1012 (8.9)	499 (73.7) 664 (10.3) 1036 (5.6)	653 0.7) 1095 9)

a) Donor number and acceptor number of the solvent: ACN (acetonitrile), 14 and 19; ACO (acetone), 17 and 13.

b) Taken from Ref. 6. c) Showing data of [Ni(acac)(tmen)]BPh₄ in Ref. 1.**Figure 2.** An ORTEP drawing of **1a**. Hydrogen atoms are omitted for clarity. Only one of two independent molecules is shown. Displacement ellipsoids are drawn at 30% probability.

larger ($>25 \text{ cm}^{-1}$) for a bidentate.^{2,10} In the spectra of **1a**, **2a**, and **3a**, there are two bands with $\Delta_{\text{NO}_3} = 49\text{--}51 \text{ cm}^{-1}$ indicating that the NO_3^- is bidentate. It is interesting to note that the difference between $\nu_{\text{C=O}}$ and $\nu_{\text{C=C}}$ of dike (Δ_{dike}) is also characteristic.^{1,5,11,12} This difference varies greatly from a square-planar structure to an octahedral one. As the Ni–O(dike) bond becomes weaker, the neighboring C=O bond becomes stronger and the C=C bond becomes weaker, therefore Δ_{dike} increases. The structures could be confirmed from this viewpoint: the Δ_{dike} values observed in the octahedral complexes **1a**, **2a**, and **3a** are larger than those of the corresponding square-planar complexes **1b**, **2b**, and **3b**.

In TG-DTA, the nitrate complexes have a melting point below 100°C . This thermal property is characteristic for

Table 3. Selected Bond Distances/ $\text{\AA}$ and Angles/ $^\circ$ of Nitrate Complexes^{a)}

	1a ^{a)}	2a	3a
Ni(1)–O(1)	2.005(2)	2.008(3)	1.978(5)
Ni(1)–O(2)	1.985(2)	1.982(3)	1.990(4)
Ni(1)–N(1)	2.147(2)	2.147(3)	2.098(7)
Ni(1)–N(2)	2.102(2)	2.081(4)	2.112(5)
Ni(1)–O(3)	2.163(2)	2.132(3)	2.126(4)
Ni(1)–O(4)	2.140(2)	2.127(3)	2.199(5)
O(1)–Ni(1)–O(2)	90.82(10)	90.67(11)	90.36(19)
N(1)–Ni(1)–N(2)	84.80(9)	85.50(14)	87.0(2)
O(3)–Ni(1)–O(4)	59.64(8)	60.29(12)	59.69(16)
O(1)–Ni(1)–N(1)	176.69(9)	179.55(13)	179.3(2)
O(2)–Ni(1)–O(3)	156.81(9)	163.19(13)	162.66(18)
N(2)–Ni(1)–O(4)	160.00(9)	158.52(15)	158.43(16)

a) Only one data of two independent molecules are shown.

this type of complexes $[\text{Ni}(\text{dike})(\text{diam})(\text{NO}_3)]$ or $[\text{Ni}(\text{dike})_2(\text{diam})]^{13}$ and in contrast to usual coordination compounds, which have rather high melting points or show decomposition at higher temperature.

X-ray Crystal Structures. Nitrate Complexes: Figure 2 shows the molecular structure of **1a**. The selected bond distances and angles of **1a–3a** are listed in Table 3. For each complex, the central nickel(II) ion is coordinated by two oxygen atoms of dike, two nitrogen atoms of diam and two oxygen atoms of nitrate to give a six-coordinated octahedral structure. The small bite angles of NO_3^- result in distorted structures. For complex **1a**, two independent molecules are observed in the crystal but no remarkable difference in the bond length or angles was observed. The Ni–donor bond distances are almost same in tmen complex **1a** and **2a**. The Ni–donor bond distances in **3a** are similar to those in $[\text{Ni}(\text{acac})(\text{dipe})(\text{NO}_3)]$ (acac = acetylacetonate).² Therefore, in octahedral

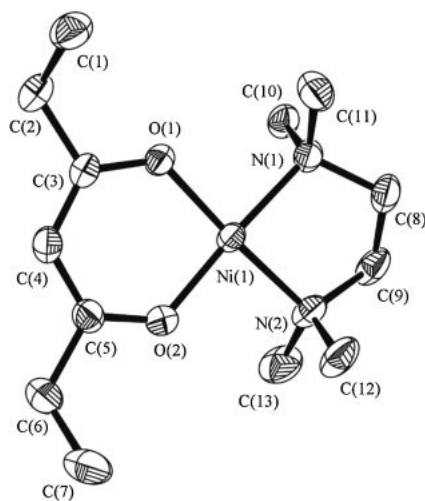


Figure 3. An ORTEP drawing of **1b**. Hydrogen atoms and counter anion are omitted for clarity. Displacement ellipsoids are drawn at 30% probability.

Table 4. Selected Bond Distances/Å and Angles/° of Tetraphenylborate Complexes

	1b	3b	4b
Ni(1)–O(1)	1.8345(16)	1.842(4)	1.848(4)
Ni(1)–O(2)	1.8409(15)	1.836(4)	1.839(4)
Ni(1)–N(1)	1.9450(18)	1.944(4)	1.967(5)
Ni(1)–N(2)	1.9404(19)	1.951(4)	1.962(5)
O(1)–Ni(1)–O(2)	95.20(7)	94.27(18)	94.47(19)
N(1)–Ni(1)–N(2)	87.82(8)	89.1(2)	89.3(2)
O(1)–Ni(1)–N(2)	176.17(6)	173.4(2)	170.2(2)
O(2)–Ni(1)–N(1)	176.40(6)	172.6(2)	171.3(2)

structures, no substituent effect of dike was observed because of the long Ni–donor bond distance.

Tetraphenylborate Complexes: Figure 3 shows the molecular structure of **1b**. The selected bond distances and angles of **1b**, **3b**, and **4b** are listed in Table 4. For each complex, the central nickel(II) ion is coordinated by two oxygen atoms of dike and two nitrogen atoms of tmen to give a four-coordinated square-planar structure. The bond distances of tmen complex **1b** are comparable to those of [Ni(acac)(tmen)]BPh₄.¹² For dipe complexes, the bond distances, particularly the Ni–N distances, in dmhd complex **4b** are longer than those in dedk complex **3b** due to the steric repulsion between dipe and dmhd. This result agrees with that of the solid reflectance spectra. The tetraphenylborate complexes with the four-coordinated square-planar structures have shorter Ni–donor bond distances than those of the octahedral nitrate complexes, which is explained by Gutmann's bond variation rules.⁵ In the solid state, the steric repulsion between bulky dipe and dike differs between dedk and dmhd, and this difference causes observable color change and the difference in bond distances, although such difference was not observed in the tmen complexes.

Solvatochromism of the Complexes in Solution. Nitrate Complexes: In the mixed-ligand complex system studied here, the major species is affected not only by the donor ability

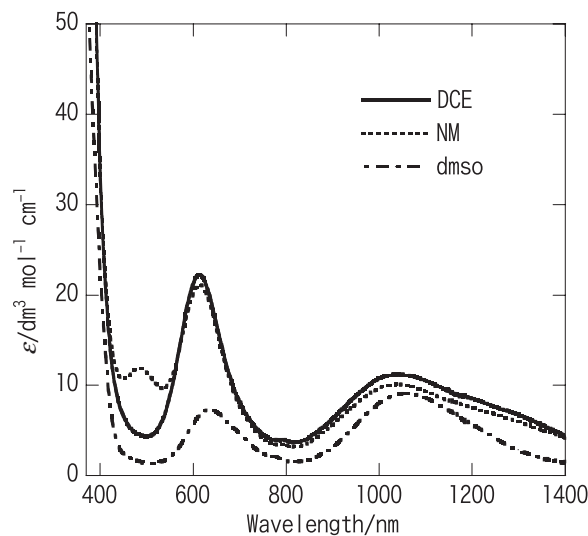


Figure 4. UV–vis spectra of [Ni(dedk)(tmen)(NO₃)] (**1a**) in various solvents.

but also by the acceptor ability of the solvent.¹ The steric effects on the solvatochromism have been investigated by UV–vis spectroscopy. Spectral data for the present complexes and the analogous acac complexes in three solvents with different donor or acceptor numbers are summarized in Table 1. The solvatochromic behavior of **3a** is not discussed because of its poor purity.

Figure 4 shows the UV–vis spectra of **1a** in 1,2-dichloroethane (DCE), nitromethane (NM), and dimethyl sulfoxide (dmso). In 1,2-dichloroethane, the spectrum has two bands whose intensities are different ($\nu_1 < \nu_2$). This means that the complex preserves an octahedral structure with the NO₃[−] ion coordinated (denoted by Oh₁ structure) the same as in the solid state. In nitromethane with acceptor ability, an additional weak absorption band due to the square-planar structure appears at 482 nm, while two bands corresponding to the octahedral species still remain. Nitromethane with poor donor ability does not coordinate to the nickel(II) ion. Therefore, the behavior of **1a** in nitromethane can be interpreted in terms of a shift of the equilibrium between square-planar (Sp) and Oh₁ species. The relative abundances of the square-planar species, x_{Sp} , in nitromethane were almost the same for **1a** (8%) and **2a** (7%).¹⁴

In a strong donor solvent, dimethyl sulfoxide, the spectrum is quite consistent with the typical spectrum of [Ni(dike)(diam)(dmso)₂]⁺.^{1–3,6,7} It is thought that two molecules of dimethyl sulfoxide replaced the NO₃[−] and coordinated (denoted by Oh₂ structure). These data suggest that there are equilibrium mixtures among three structures; Sp, Oh₁, and Oh₂ in these solutions illustrated in Scheme 1. The peak positions of **1a** and **2a** in the three solvents are almost the same as those of [Ni(acac)(tmen)(NO₃)],¹ which means that the solvatochromism of these complexes is explained in terms of the same type of solute–solvent interaction. For tmen complexes [Ni(dike)(tmen)(NO₃)], the steric crowding effect of dike was not observed in solution.

Tetraphenylborate Complexes: Complexes **1b–4b** showed solvatochromism due to the “solute–solvent interaction.” Spectral data for these complexes and analogous acac

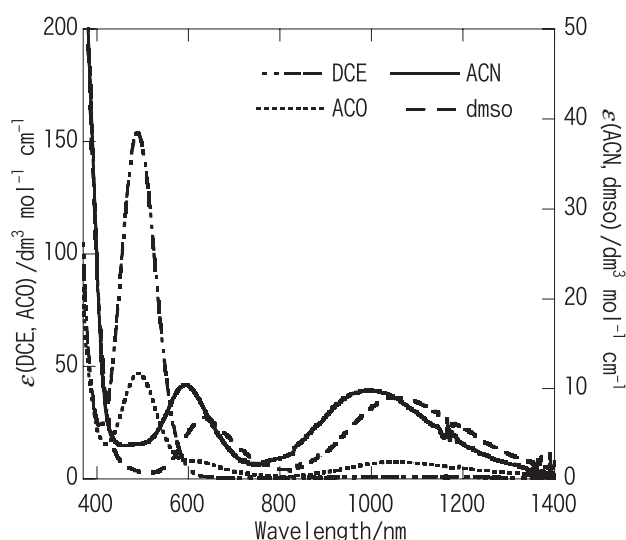
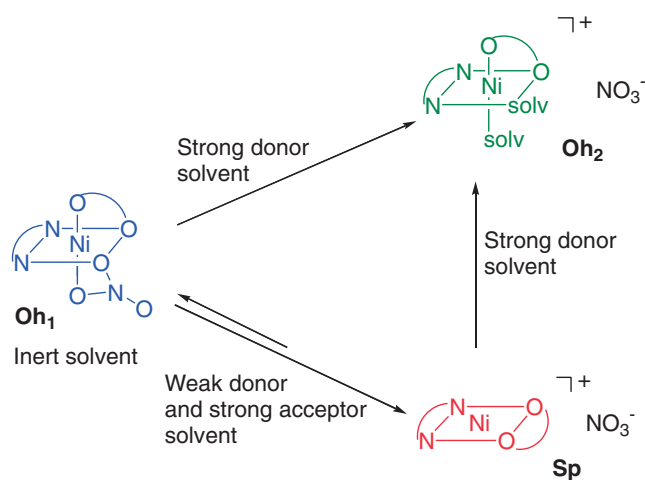
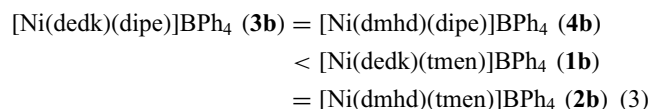


Figure 5. UV-vis spectra of $[\text{Ni}(\text{dedk})(\text{tmen})]\text{BPh}_4$ (**1b**) in various solvents.

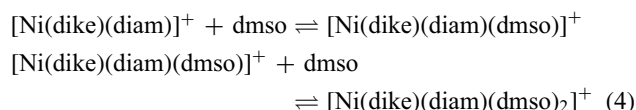
complexes are summarized in Table 2. Figure 5 shows the UV-vis spectra and color variations of **1b** in 1,2-dichloroethane, acetonitrile (ACN), acetone (ACO), and dimethyl sulfoxide. In 1,2-dichloroethane, the solution is red, and the spectrum shows a strong absorption band at 489 nm ($\epsilon = 158 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), indicating that **1b** has a square-planar stereochemistry. On the other hand, the solution is green in dimethyl sulfoxide, showing two relatively weak bands at 1055 and 635 nm ($\epsilon = 9.1$ and $6.8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively). This means that two molecules of dimethyl sulfoxide are coordinated to the nickel(II) center to form an octahedral geometry, i.e., the equilibrium of $\text{Sp} \rightleftharpoons \text{Oh}$ is shifted to the right. In solvent with a medium donor ability, such as acetone (ACO), the spectrum shows a band at 491 nm and a relatively weak band at 1050 nm and shoulder around 625 nm, indicating that both square-planar and octahedral species coexist in the solution. The spectrum of **1b** in acetonitrile (ACN) shows only the bands due to the octahedral species, which is not consistent with the expectations for DN ($\text{ACO} > \text{ACN}$). The acetonitrile molecule is not affected by the steric hindrance of the complex

because of its linear and slim shape. Therefore the acetonitrile can easily coordinate to the nickel(II) center.^{1,3} In addition, the nitrogen donor atom in acetonitrile causes blue-shift of the two bands of the octahedral species compared with those observed in other solvents with oxygen donor atoms.^{1,3,12} For other complexes **2b**, **3b**, and **4b**, the major components in each solvent evaluated from the UV-vis spectrum are same as that of **1b**. The ligand field strengths of the square-planar complexes are ordered on the basis of the λ_{max} values in 1,2-dichloroethane as follows:



The difference between [**1b**, **2b**] and [**3b**, **4b**] is due to the diamine ligands as observed in the solid state (eq 2). Interestingly, the difference between **3b** and **4b** observed in the solid state disappeared, that is, their ligand field strengths are the same in 1,2-dichloroethane.

Adduct Formation with dmsO: When dimethyl sulfoxide was added to the tetraphenylborate complex in an inert solvent, 1,2-dichloroethane, the Sp species forms a five- and six-coordinated complexes as represented by eq 4.



$$\begin{aligned}
 K_1 / \text{mol dm}^{-3} &= C_{[\text{Ni}(\text{dike})(\text{diam})(\text{dmsO})]} / (C_{[\text{Ni}(\text{dike})(\text{diam})]} C_{\text{dmsO}}) \\
 K_2 / \text{mol dm}^{-3} &= C_{[\text{Ni}(\text{dike})(\text{diam})(\text{dmsO})_2]} / (C_{[\text{Ni}(\text{dike})(\text{diam})(\text{dmsO})]} C_{\text{dmsO}}) \\
 \log \beta &= \log K_1 + \log K_2 \text{ (5)}
 \end{aligned}$$

The spectral changes associated with the addition of dimethyl sulfoxide are shown in Figure 6 (for **1b**) and Figure 7 (for **3b**). The variation in the spectra for **2b** and **4b** are similar to those for **1b** and **3b**, respectively. In the cases of **1b** and **2b** (Figure 6), the absorbance at 489 nm corresponding to the square-planar species decreases and those at 635 and 1055 nm corresponding to the octahedral species increase with the addition of dimethyl sulfoxide. For dipe complexes **3b** and **4b** (Figure 7), absorptions attributed to a five-coordinated intermediate were observed around 1400, 900, 650, and 400 nm at the beginning of the addition of dimethyl sulfoxide and their intensities decreased on further addition of dimethyl sulfoxide. The calculated spectrum of the five-coordinated intermediate for complex **3b** (Figure S5) agrees well with that of $[\text{Ni}(\text{Me}_6\text{tren})\text{Cl}]\text{Cl}$ where Me_6tren is 2,2',2''-tri(*N,N*-dimethylamino)triethylamine with the five-coordinated trigonal-bipyramidal structure.¹⁵ The primary coordination of dimethyl sulfoxide gives the five-coordinated trigonal-bipyramidal structure and then the *cis*-octahedral structure is favored to form by coordination of second dimethyl sulfoxide molecule as shown in Scheme 2. This result confirms the reaction scheme proposed by Linert et al.⁶ for the first time by spectroscopy. It is notable that the five-coordinated structure with one solvent molecule is stable enough to be captured during titration. In the series of $\text{Ni}(\text{dike})(\text{diam})\text{X}$, so far the coordination of the two solvent molecules has been observed to form the octahedral complex (Oh_2) and the spectral pattern due to only the square-planar and octahedral species are

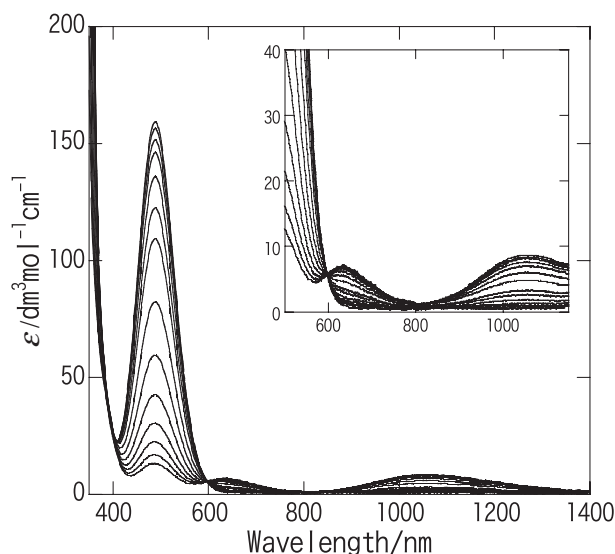


Figure 6. Spectral change of [Ni(dedk)(tmen)]BPh₄ (**1b**) in 1,2-dichloroethane on addition of dmsol at 300 K. Concentrations of complex are 6.6×10^{-3} – 5.9×10^{-3} mol dm⁻³ and concentrations of dmsol are 0–0.035 mol dm⁻³ from the top to the bottom.

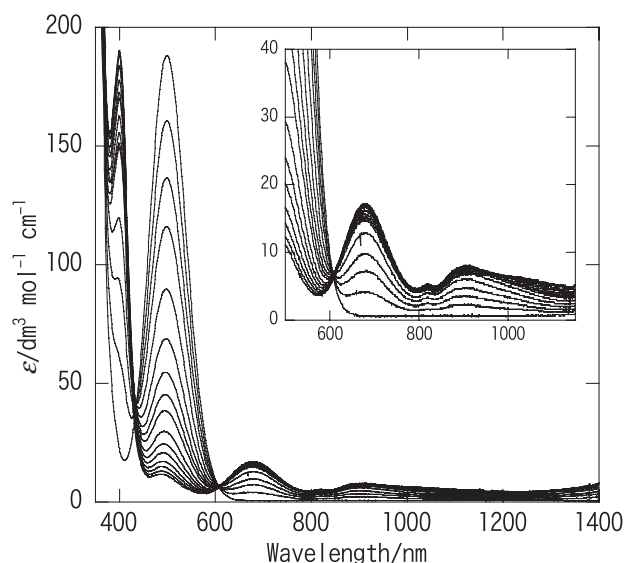
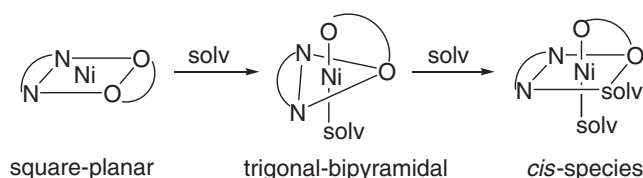


Figure 7. Spectral change of [Ni(dedk)(dipe)]BPh₄ (**3b**) in 1,2-dichloroethane on addition of dmsol at 300 K. Concentrations of complex are 5.1×10^{-3} – 4.1×10^{-3} mol dm⁻³ and concentrations of dmsol are 0–0.057 mol dm⁻³ from the top to the bottom.

observed as shown in Figure 6.^{3,6,16} Even when a halide or pseudohalide anion is used for counter anion X, no five-coordinated species were obtained in solid states, and the five-coordinated structures formed in solutions are unstable and rapidly disproportionate to [Ni(dike)₂(diam)] and [Ni(diam)X₂].¹⁷

Comparison of Equilibrium Constants: The equilibrium constants defined in eq 5 were determined in 1,2-dichloroethane at 300 K and are listed in Table 5. The orders of equilibrium constants are summarized in eqs 6–8.



Scheme 2.

Table 5. Equilibrium Constants (300 ± 0.5 K)

Complex	log K_1	log K_2	K_1/K_2	log β
1b	1.4 ± 0.1	2.8 ± 0.1	0.040	4.29 ± 0.03
2b	1.3 ± 0.2	2.9 ± 0.2	0.025	4.25 ± 0.04
3b	2.72 ± 0.02	1.23 ± 0.06	30.9	3.95 ± 0.06
4b	2.498 ± 0.004	1.34 ± 0.01	14.4	3.84 ± 0.01

$$\begin{aligned}
 \log K_1: & [\text{Ni}(\text{dedk})(\text{tmen})]\text{BPh}_4 \text{ (**1b**)} \\
 &= [\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4 \text{ (**2b**)} \\
 &\ll [\text{Ni}(\text{dmhd})(\text{dipe})]\text{BPh}_4 \text{ (**4b**)} \\
 &< [\text{Ni}(\text{dedk})(\text{dipe})]\text{BPh}_4 \text{ (**3b**)} \quad (6)
 \end{aligned}$$

$$\begin{aligned}
 \log K_2: & [\text{Ni}(\text{dedk})(\text{dipe})]\text{BPh}_4 \text{ (**3b**)} \\
 &= [\text{Ni}(\text{dmhd})(\text{dipe})]\text{BPh}_4 \text{ (**4b**)} \\
 &< [\text{Ni}(\text{dedk})(\text{tmen})]\text{BPh}_4 \text{ (**1b**)} \\
 &= [\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4 \text{ (**2b**)} \quad (7)
 \end{aligned}$$

$$\begin{aligned}
 \log \beta: & [\text{Ni}(\text{dedk})(\text{dipe})]\text{BPh}_4 \text{ (**3b**)} \\
 &= [\text{Ni}(\text{dmhd})(\text{dipe})]\text{BPh}_4 \text{ (**4b**)} \\
 &< [\text{Ni}(\text{dedk})(\text{tmen})]\text{BPh}_4 \text{ (**1b**)} \\
 &= [\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4 \text{ (**2b**)} \quad (8)
 \end{aligned}$$

The order of log K_1 values means that the primary coordination of dimethyl sulfoxide to the dipe complexes **3b** and **4b** occurs more easily than that to the corresponding tmen complexes **1b** and **2b**. This is rationalized in terms of the difference of the ligand field strengths shown in eq 3. No difference was observed between **1b** and **2b** because there is no steric effect of dike as mentioned above. On the other hand, log K_1 of **4b** is smaller than that of **3b**, indicating that the square-planar structure of **4b** is more stable than that of **3b**. Since the ligand field strengths of the two complexes in 1,2-dichloroethane are the same as shown in eq 3, the difference in log K_1 arises from the difference in the steric crowding effect of dike. The nickel(II) center is shielded from the solvent by bulky piperidine rings in dipe and isopropyl groups in dmhd.

The log K_2 values are usually much larger than the log K_1 values in the coordination of dimethyl sulfoxide to [Ni(dike)-(diam)]BPh₄ including [Ni(acac)(dipe)]BPh₄.⁶ The log K_2 values of **1b** and **2b** are also larger than their log K_1 values, hence only the absorptions due to the square-planar and octahedral species were observed in the titration spectra as shown above. In dipe complexes, inverse results were obtained: log $K_1 > \log K_2$. The secondary coordination of dimethyl sulfoxide to the nickel(II) center is inhibited by the existing ligands (including one dmso molecule). The log K_2 values of **3b** and **4b** are almost the same. The steric hindrances of dike may not affect the change from five-coordinated structure to octahedral structure due to long Ni–donor bond lengths. This

assumption is supported by similarity of the calculated spectra of the five-coordinated species derived from **3b** and **4b**. The higher stability of the five-coordinated structure in **3b** (K_1/K_2 : **3b** > **4b**) is due to the difference of the relative stabilities of the square-planar structures.

The order of the $\log \beta$ values conflicts with the expectation from the ligand field strengths in 1,2-dichloroethane (eq 3). In the acac complexes $\text{Ni}(\text{acac})(\text{tmen}/\text{dipe})\text{X}$ ($\text{X} = \text{NO}_3^-$, BF_4^-), the ligand field strength of the dipe complex is smaller than that of the tmen complex and the octahedral structure of the dipe complex is more stable than that of the tmen complex in solvatochromism.^{2,6} The bulkiness and rigidity of dipe is effective, but the effect of the ligand field strength when the dike is acac, which is weaker and less bulky donor than dedk or dmhd. In the cases of the present dedk or dmhd complex, the steric effect of dipe and dike is stronger than the effect of the ligand field strengths. Therefore the reactions into the octahedral structure are unfavorable in **3b** and **4b** due to the steric effect in spite of their weak ligand field strengths as compared with **1b** and **2b**.

Experimental

Materials. All chemicals were commercially available from Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., and Sigma-Aldrich Co. and were used without further purification. Solvents for spectral measurements were "spectro-grade."

Physical Measurements. Elemental analyses (C, H, N) were measured on a Perkin-Elmer 2400 CHN analyzer. IR spectra were obtained as KBr pellets on a Perkin-Elmer FT-IR SPECTRUM 2000. Melting points were obtained by thermal analyses (TG-DTA), which were carried out using a Shimadzu thermal analyzer (DTG-50). Mass spectra were obtained on a JEOL JMS-700 Mstation in the fast atom bombardment (FAB) mode using ultramark as standard and 3-nitrobenzyl alcohol (NBA) as matrix, in which the tetraphenylborate complexes are decomposed during measurements. Magnetic data were measured on a Shimadzu Torsion Magnetometer MB-100 at room temperature and the effective magnetic moments (μ_{eff}) were calculated with correcting $\chi_{\text{diamagnetic}}$. UV-vis spectra were obtained on a Shimadzu UV-3100PC Spectrophotometer using a 1 cm quartz cell. Solid reflectance spectra were recorded on the Shimadzu UV-3100PC Spectrophotometer using an integration sphere and barium sulfate as reference.

Synthesis of Nitrate Complexes. To an ethanol solution (20 mL) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 mmol), Hdike (5 mmol), and Et_3N (5 mmol) were added, followed by the addition of diam (5 mmol) to give a deep green solution (this mixture is denoted "ethanol solution [A]"). After concentration of the solution with cooling, a blue-green powdery or crystalline solid was obtained. The powder was recrystallized from 1,2-dichloroethane. Yield 50–60%. Although the formation of $[\text{Ni}(\text{dmhd})(\text{dipe})(\text{NO}_3)]$ was confirmed by the absorption peaks in UV-vis spectra in the ethanol solution, concentration of this solution gave not the desired nitrate complex but powder of a bis-dmhd complex $[\text{Ni}(\text{dmhd})_2(\text{dipe})]$.

[Ni(dedk)(tmen)(NO₃)] (1a): Blue. Anal. Found: C, 42.81; H, 7.56; N, 11.57%. Calcd for $\text{C}_{13}\text{H}_{27}\text{N}_3\text{NiO}_5$: C, 42.89; H, 7.48; N, 11.54%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 1036, 617. Selected

IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1597, 1515 cm^{-1} ($\Delta_{\text{dike}} = 82 \text{ cm}^{-1}$); combination bands of bidentate NO_3^- 1765, 1717 cm^{-1} ($\Delta_{\text{NO}_3} = 48 \text{ cm}^{-1}$). Mp/ $^\circ\text{C}$: 71. FAB⁺ MS: 302 $[\text{M} + \text{H} - \text{NO}_3]^+$ (calcd 302). $\mu_{\text{eff}}/\text{BM}$: 3.23.

[Ni(dmhd)(tmen)(NO₃)] (2a): Blue. Anal. Found: C, 45.42; H, 8.05; N, 10.36%. Calcd for $\text{C}_{15}\text{H}_{31}\text{N}_3\text{NiO}_5$: C, 45.94; H, 7.97; N, 10.72%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 1034, 612. Selected IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1601, 1531 cm^{-1} ($\Delta_{\text{dike}} = 70 \text{ cm}^{-1}$); combination bands of bidentate NO_3^- 1770, 1719 cm^{-1} ($\Delta_{\text{NO}_3} = 51 \text{ cm}^{-1}$). Mp/ $^\circ\text{C}$: 77. FAB⁺ MS: 330 $[\text{M} + \text{H} - \text{NO}_3]^+$ (calcd. 330). $\mu_{\text{eff}}/\text{BM}$: 3.21.

[Ni(dedk)(dipe)(NO₃)] (3a): Pale Blue. Anal. Found: C, 49.19; H, 7.82; N, 9.23%. Calcd for $\text{C}_{19}\text{H}_{35}\text{N}_3\text{NiO}_5$: C, 51.38; H, 7.94; N, 9.46%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 1066, 621. Selected IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1599, 1519 cm^{-1} ($\Delta_{\text{dike}} = 79 \text{ cm}^{-1}$); combination bands of bidentate NO_3^- 1774, 1725 cm^{-1} ($\Delta_{\text{NO}_3} = 49 \text{ cm}^{-1}$). Mp/ $^\circ\text{C}$: 93. FAB⁺ MS: 381 $[\text{M} - \text{NO}_3]^+$ (calcd 381). $\mu_{\text{eff}}/\text{BM}$: 3.39.

Synthesis of Tetraphenylborate Complexes. The complexes were prepared by anion-exchange from nitrate complexes. Sodium tetraphenylborate (8 mmol) in ethanol was added to the "ethanol solution [A]." After stirring the solution for twenty minutes, the red-violet precipitate was collected and recrystallized from 1,2-dichloroethane to give crystals. The crystal was used for X-ray structure analysis except for $[\text{Ni}(\text{dmhd})(\text{tmen})]\text{BPh}_4$ (**2b**). Yield 52–68%.

[Ni(dedk)(tmen)]BPh₄ (1b): Bright red. Anal. Found: C, 71.19; H, 7.69; N, 4.63%. Calcd for $\text{C}_{37}\text{H}_{47}\text{BN}_2\text{NiO}_2$: C, 71.53; H, 7.63; N, 4.51%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 490. Selected IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1566, 1527 ($\Delta_{\text{dike}} = 39 \text{ cm}^{-1}$). FAB⁺ MS: 302 $[\text{M} + \text{H} - \text{BPh}_4]^+$ (calcd 302). Diamagnetic.

[Ni(dmhd)(tmen)]BPh₄ (2b): Bright red. Anal. Found: C, 72.66; H, 8.27; N, 4.63%. Calcd for $\text{C}_{39}\text{H}_{51}\text{BN}_2\text{NiO}_2$: C, 72.14; H, 7.92; N, 4.32%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 493. Selected IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1580, 1532 ($\Delta_{\text{dike}} = 48 \text{ cm}^{-1}$). FAB⁺ MS 330 $[\text{M} + \text{H} - \text{BPh}_4]^+$ (calcd 330). Diamagnetic.

[Ni(dedk)(dipe)]BPh₄ (3b): Reddish pink. Anal. Found: C, 73.50; H, 8.04; N, 4.08%. Calcd for $\text{C}_{43}\text{H}_{55}\text{BN}_2\text{NiO}_2$: C, 73.63; H, 7.90; N, 3.99%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 505. Selected IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1565, 1525 ($\Delta_{\text{dike}} = 40 \text{ cm}^{-1}$). FAB⁺ MS: 381 $[\text{M} - \text{BPh}_4]^+$ (calcd 381). Diamagnetic.

[Ni(dmhd)(dipe)]BPh₄ (4b): Violet. Anal. Found: C, 73.88; H, 8.30; N, 3.90%. Calcd for $\text{C}_{45}\text{H}_{59}\text{BN}_2\text{NiO}_2$: C, 74.09; H, 8.15; N, 3.84%. Solid reflection $\lambda_{\text{max}}/\text{nm}$: 519. Selected IR bands/ cm^{-1} : $\nu_{\text{C=O}} + \nu_{\text{C=C}}$ 1561, 1535 ($\Delta_{\text{dike}} = 26 \text{ cm}^{-1}$). FAB⁺ MS: 409 $[\text{M} - \text{BPh}_4]^+$ (calcd 409). Diamagnetic.

X-ray Crystallography. X-ray data of complexes were collected on a Mac Science M03XHF four-circle diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The structures were solved by a direct method using SIR92,¹⁸ and refined by full-matrix least-square techniques with SHELXL97.¹⁹ All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. C(1) and C(15)–C(19) in **3a**, C(7) in **3b**, and C(1), C(2), C(8), and C(9) in **4b** were disordered and located in two positions. All calculations were performed using maxus²⁰ and WinGX.²¹ Crystallographic data and refinement parameters are listed in Table 6.

Table 6. Crystallographic Data

	[Ni(dedk)(tmen)(NO ₃)]	[Ni(dmhd)(tmen)(NO ₃)]	[Ni(dedk)(dipe)(NO ₃)]	[Ni(dedk)(tmen)]BPh ₄	[Ni(dedk)(dipe)]BPh ₄	[Ni(dmhd)(dipe)]BPh ₄
	1a	2a	3a	1b	3b	4b
Formula	C ₁₃ H ₂₇ N ₃ NiO ₅	C ₁₅ H ₃₁ N ₃ NiO ₅	C ₁₉ H ₃₅ N ₃ NiO ₅	C ₃₇ H ₄₇ BN ₂ NiO ₂	C ₄₃ H ₅₅ BN ₂ NiO ₂	C ₄₅ H ₅₉ BN ₂ NiO ₂
Molecular weight	364.07	392.12	444.19	621.27	701.39	729.43
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1	<i>Cc</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	15.760(7)	7.588(5)	8.483(5)	9.998(5)	12.384(7)	9.792(5)
<i>b</i> /Å	14.074(5)	14.863(5)	10.281(3)	12.783(15)	18.450(6)	22.682(6)
<i>c</i> /Å	17.338(6)	18.445(3)	13.948(4)	14.330(6)	17.185(4)	18.390(3)
α /°	90	90	77.43(2)	79.85(6)	90	90
β /°	109.23(3)	92.16(3)	89.39(4)	80.03(4)	96.30(3)	92.63(2)
γ /°	90	90	75.30(3)	73.03(6)	90	90
<i>V</i> /Å ³	3631(2)	2078.8(15)	1147.1(8)	1701(2)	3903(3)	4080(2)
<i>Z</i>	8	4	2	2	4	4
<i>D</i> _{calcd} /g cm ⁻³	1.332	1.253	1.286	1.207	1.194	1.188
Crystal size/mm ³	0.75 × 0.75 × 0.35	0.80 × 0.70 × 0.50	0.50 × 0.15 × 0.13	0.75 × 0.50 × 0.50	0.75 × 0.25 × 0.13	0.30 × 0.25 × 0.20
μ /mm ⁻¹	1.092	0.959	0.877	0.601	0.534	0.513
Total reflections	7046	4087	4091	8031	4309	6219
Unique reflections	6805	3802	3816	7683	4309	6030
Observed reflections	6503	3552	3233	7486	3962	5096
<i>R</i> 1 [<i>F</i> _o ² > 2σ(<i>F</i> _o ²)]	0.0500	0.0608	0.0790	0.0429	0.0498	0.0897
<i>wR</i> 2 (all data)	0.1287	0.1648	0.1886	0.1202	0.1154	0.1714
Goodness of fit	1.043	0.996	1.006	1.083	1.006	1.013
Reflection/Parameter ratio	17.10	17.44	12.43	19.75	9.53	13.28

Crystal data have been submitted to CCDC; the document numbers are 723549 (**1a**), 723551 (**2a**), 723552 (**3a**), 723550 (**1b**), 723553 (**3b**), and 723554 (**4b**). Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing: data_request@ccdc.cam.ac.uk, or contacting CCDC, 12, Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44 1223 336033).

Equilibrium Constants. The equilibrium constants defined by eq 5 were determined by spectrophotometric titration at 300 K. A 1,2-dichloroethane solution of dimethyl sulfoxide was successively added to a 1,2-dichloroethane solution ($6 \times 10^{-3} \text{ mol dm}^{-3}$) of the complex $[\text{Ni}(\text{dike})(\text{diam})]\text{BPh}_4$ and the UV-vis spectra were recorded. The obtained series of spectra were fitted to a two-step reaction scheme using SPECFIT program to evaluate the equilibrium constants.²² The component spectrum of the five-coordinated species was also obtained in the curve-fitting process.

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Supporting Information

ORTEP drawings of the X-ray structure of **2a**, **3a**, **3b**, and **4b** are shown in Figures S1, S2, S3, and S4, respectively. Figure S5 is the calculated spectra of the 5-coordinated complex. These materials are available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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