

Alkyl-Substitution Effect of the Diamine on Coordination Geometry and Ligand-Field Strength of Nickel(II) Mixed-Ligand Complexes Containing *N*-Alkylethylenediamine, Acetylacetonate, and Nitrate Ligands[#]

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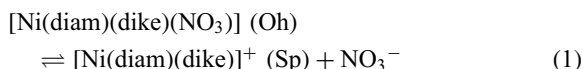
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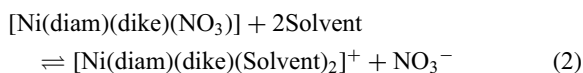
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Structures and spectral properties have been investigated for nickel(II) mixed-ligand complexes, [Ni(Me₄en)(acac)(NO₃)] (**1**), [Ni(EtMe₃en)(acac)(NO₃)] (**2**), [Ni(*asym*-Et₂Me₂en)(acac)(NO₃)] (**3**), [Ni(Et₃Meen)(acac)(NO₃)] (**4**), and [Ni(Et₄en)(acac)(NO₃)] (**5**) (Me₄en = *N,N,N',N'*-tetramethylethylenediamine, EtMe₃en = *N*-ethyl-*N',N',N'*-trimethylethylenediamine, *asym*-Et₂Me₂en = *N,N*-diethyl-*N',N'*-dimethylethylenediamine, Et₃Meen = *N,N,N'*-triethyl-*N'*-methylethylenediamine, Et₄en = *N,N,N',N'*-tetraethylethylenediamine, acac = acetylacetonate). The crystal structures of complexes **2** and **3** have been determined. These complexes have 6-coordinated octahedral (Oh) structure with a bidentate nitrate in the solid state as well as in 1,2-dichloroethane or acetone solution, while the nitrate partially dissociates in nitromethane to establish an equilibrium with square-planar (Sp) form [Ni(acac)(diam)]⁺ where diam represents a diamine. The degree of dissociation of NO₃[−] increases in the order of diam: Me₄en < EtMe₃en < *asym*-Et₂Me₂en < Et₃Meen < Et₄en, indicating that the bulkier diamine more favors the Sp form. This relative stabilization of the Sp form can be attributed to relief of the steric strain in the Oh species. Effects of bulky substituents in the diamine on the ligand-field strength are also discussed.

In our previous work, we investigated structure and spectral properties for a series of mixed-ligand nickel(II) complexes with an *N*-(and *N'*)-alkylated ethylenediamine (diam) and β-diketonate (dike) ligands, Ni(diam)(dike)X, where X represents an anion.^{1–4} The coordination structure of this type of complex varies with the donor ability of the anion and solvent. Nitrate complexes [Ni(diam)(dike)(NO₃)], in particular, are soluble in both polar and nonpolar solvents and exhibit solvatochromism due to an equilibrium between the octahedral (Oh) and the square-planar (Sp) forms as represented by eq 1.



When the solvent has high donor ability, another octahedral species may be formed by ligand exchange as shown in eq 2.



Since solvent–solute interactions play an important role in such equilibria, the solvatochromic properties are primarily determined by properties such as dielectric constant, donor number (DN), and acceptor number (AN)⁵ of the solvent. Additionally, the steric and electronic properties of the ligands should affect solvatochromic behavior through inter-ligand repulsion, trans influence, ligand-field stabilization energy (LFSE), etc. Specifically, variation in bulkiness of substituents on the ligand(s) may influence the equilibrium between the Oh and Sp forms in two opposite ways: With an increase in the bulkiness, (i) the Oh form can more dominate due to decrease of LFSE or (ii) the

Sp form can be more favored because the Oh form should be more destabilized due to the more severe inter-ligand repulsion.

Toward comprehensive understanding of the solution equilibria such as eqs 1 and 2, we have investigated a series of [Ni(diam)(acac)(NO₃)], complexes **1–5**, in which the number of Et/Me groups on the nitrogen atoms in diam is systematically varied (Figure 1). In the present paper, we report the structure

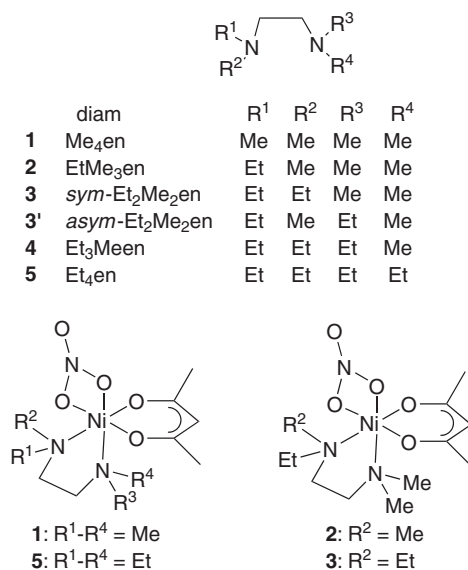


Figure 1. Substituents in diamines and structures of complexes.

and spectroscopic properties of **1–5** in the solid state and in various solvents. From the results of UV–vis spectra and electric conductivity measurements, we discuss the effects of the substituents in diam on the above equilibrium (eq 1) in nitromethane solution.

Experimental

Materials. *N,N,N',N'*-Tetramethylethylenediamine (Me₄en), *N,N,N',N'*-tetraethylethylenediamine (Et₄en), nickel(II) nitrate hexahydrate, and acetylacetone were commercially available. All reagents were used without further purification. [Ni(Me₄en)(acac)(NO₃)] (**1**) and [Ni(Et₄en)(acac)(NO₃)] (**5**) were synthesized as previously reported.^{1,2} Solvents of spectro-grade and analytical grade were used for spectral and electrical measurements, respectively.

Physical Measurements. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer. Infrared spectra were measured with a Perkin-Elmer FT-IR SPECTRUM 2000 as KBr disks. Mass spectra were obtained on a JEOL JMS-700 Mstation in the positive fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol as matrix. UV–vis spectra were recorded on a Shimadzu UV-3100PC spectrophotometer at a concentration of 2.5×10^{-2} mol dm⁻³ at room temperature. Electric conductance was measured with a Conductivity Outfit Model AOC-10 (Denki-Kagaku-Keiki Co., Ltd.) at 25.0 ± 0.1 °C at a concentration of 2.5×10^{-2} mol dm⁻³. ¹H NMR spectra (400 MHz) were measured on a JEOL JNM-AL400 spectrometer in CDCl₃.

Syntheses of Ligands and Complexes 2–4. *N*-Ethyl-*N,N',N'*-trimethylethylenediamine (EtMe₃en):^{6,7} *N*-Ethylethylenediamine (4.4 g, 50 mmol) and HCHO (35% aqueous solution, 14.2 g, 165 mmol) were added to HCOOH (17.2 g, 375 mmol) in an ice bath, and the resultant mixture was refluxed for 24 h. The solution was cooled to 25 °C and made basic with 2 M aqueous NaOH. To this mixture, KOH pellets were added until the product was separated. The liberated amine was extracted with Et₂O (25 mL $\times$ 5) and the organic extracts were dried over MgSO₄. After removing the solvent by rotary evaporation, yellow oil was obtained. Yield 54%. ¹H NMR: δ 1.060 (t, 3H), 2.24 (9H, NCH₃ $\times$ 3), 2.44 (m, 6H).

N,N'-Diethyl-*N,N'*-dimethylethylenediamine (*sym*-Et₂Me₂en): *N,N'*-Diethylethylenediamine was methylated as described for EtMe₃en. Yield 55%. ¹H NMR δ 1.059 (t, 6H), 2.236 (s, 6H), 2.43 (m, 8H).

N,N'-Diethyl-*N,N'*-dimethylethylenediamine (*asym*-Et₂Me₂en): *N,N'*-Diethylethylenediamine was methylated as described for EtMe₃en. Yield 70%. ¹H NMR δ 1.033 (t, 6H), 2.245 (s, 6H), 2.40 (m, 2H), 2.56 (m, 6H).

N,N,N'-Triethyl-*N'*-methylethylenediamine (Et₃Meen): *N,N,N'*-Triethylethylenediamine was methylated as described for EtMe₃en. Yield 60%. ¹H NMR δ 1.049 (9H, CH₃ $\times$ 3), 2.238 (s, 3H), 2.44 (m, 4H), 2.56 (m, 6H).

[Ni(EtMe₃en)(acac)(NO₃)] (**2**): To an ethanol solution of Ni(NO₃)₂·6H₂O (2.91 g, 10 mmol), acetylacetone (1.00 g, 10 mmol), and triethylamine (1.01 g, 10 mmol) were added. To this solution EtMe₃en (10 mmol in ethanol) was added dropwise with vigorous stirring. The resultant green solution was evaporated with a rotary evaporator, and the residue was recrystallized from 1,2-dichloroethane (DCE) twice. Green crystals were obtained. Yield 86%. Anal. Found: C, 41.04; H, 7.42; N, 11.99%. Calcd for C₁₂H₂₅N₃NiO₅: C, 41.18; H, 7.20; N, 12.00%. FAB-MS: m/z 287 ([Ni(EtMe₃en)(acac)]⁺). Single crystals suitable for X-ray diffrac-

tion study were grown from the DCE solution kept in a freezer for several days.

[Ni(*asym*-Et₂Me₂en)(acac)(NO₃)] (**3**): **3** was obtained by the same procedures using *asym*-Et₂Me₂en. Yield 53%. Anal. Found: C, 42.78; H, 7.61; N, 11.54%. Calcd for C₁₃H₂₇N₃NiO₅: C, 42.89; H, 7.48; N, 11.54%. FAB-MS: m/z 301 ([Ni(Et₂Me₂en)(acac)]⁺). Single crystals suitable for X-ray analysis were grown from the DCE solution kept in a freezer for several days.

[Ni(*sym*-Et₂Me₂en)(acac)(NO₃)] (**3'**): **3'** synthesis was tried by the same procedures using *sym*-Et₂Me₂en, but product was obtained only as crude (purity: ca. 90%) due to difficulty in crystallization. FAB-MS: m/z 301 ([Ni(Et₂Me₂en)(acac)]⁺).

[Ni(Et₃Meen)(acac)(NO₃)] (**4**): **4** was obtained by the same procedures using Et₃Meen. Yield 46%. Anal. Found: C, 42.96; H, 7.76; N, 11.58%. Calcd for C₁₄H₂₉N₃NiO₅·0.5H₂O: C, 43.44; H, 7.81; N, 10.86%. FAB-MS: m/z 315 ([Ni(Et₃Meen)(acac)]⁺).

X-ray Crystallography. Intensity data of complexes **2** and **3** were collected by the ω -2 θ scan technique on a MacScience M03XHF four-circle diffractometer with graphite-monochromatized Mo K α radiation (λ = 0.71073 Å) at 298 K. The intensities were corrected for Lorentz and polarization effects and semi-empirical absorption correction was applied using ψ -scans. The structure was solved by the direct method with SIR92⁸ and refined by full-matrix least-squares techniques with SHELX97.⁹ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions. All drawing and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan). Crystallographic data and refinement parameters are listed in Table 1. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. The document numbers are 704827 (**2**) and 704826 (**3**). Copies of the data can be obtained free of charge via <http://www.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

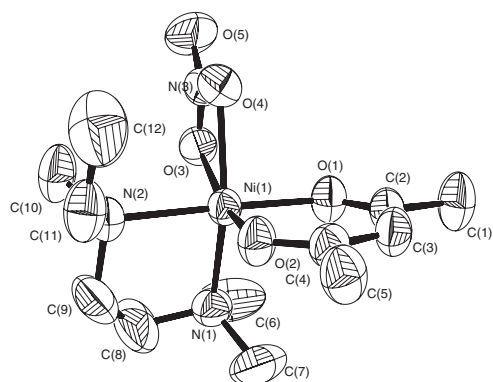
Table 1. Crystallographic Data and Details of Data Collection and Refinement

	2	3
Crystal color	green	green
Formula	C ₁₂ H ₂₅ N ₃ NiO ₅	C ₁₃ H ₂₇ N ₃ NiO ₅
Crystal dimensions /mm ³	0.75 $\times$ 0.38 $\times$ 0.25	0.93 $\times$ 0.50 $\times$ 0.38
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.847(6)	10.064(3)
<i>b</i> /Å	10.830(7)	10.930(5)
<i>c</i> /Å	17.39(2)	17.831(8)
β /°	113.6(2)	114.81(7)
<i>V</i> /Å ³	1700.0(2)	1780.4(13)
<i>Z</i>	4	4
<i>D</i> _{calcd} /Mg m ⁻³	1.368	1.358
μ /mm ⁻¹	1.164	1.114
θ _{max} /°	27.51	27.52
No. of reflections used	3339	3714
No. of parameters	190	200
<i>R</i>	0.0581	0.0604
<i>R</i> _w	0.1535	0.1581
<i>S</i>	1.059	1.112

Table 2. Characteristic IR Absorption Frequencies (cm^{-1})^{a)}

	$\nu_{\text{NO}_3}/\text{cm}^{-1}$		$\Delta\nu_{\text{NO}_3}$
[Ni(Me ₄ en)(acac)(NO ₃)] (1)	1771	1723	48
[Ni(EtMe ₃ en)(acac)(NO ₃)] (2)	1771	1720	51
[Ni(<i>asym</i> -Et ₂ Me ₂ en)(acac)(NO ₃)] (3)	1771	1720	51
[Ni(<i>sym</i> -Et ₂ Me ₂ en)(acac)(NO ₃)] (3')	1768	1723	45
[Ni(Et ₃ Meen)(acac)(NO ₃)] (4)	1771	1723	48
[Ni(Et ₄ en)(acac)(NO ₃)] (5)	1776	1726	50

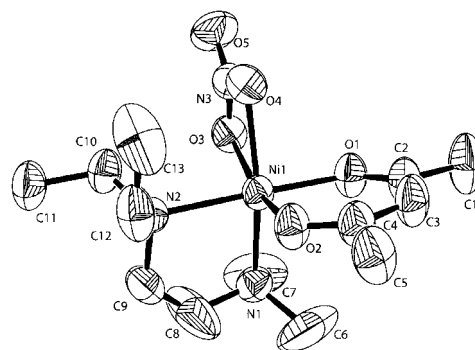
a) Measured as a KBr disk.

**Figure 2.** ORTEP drawing of [Ni(EtMe₃en)(acac)(NO₃)] (**2**). Displacement ellipsoids are drawn with 50% probability. H-atoms are excluded for clarity.

Results and Discussion

Structure of Complexes 1–5 in the Solid State. Complexes **1–5** are green in color, suggesting that each of them has an octahedral coordination sphere consisting of two nitrogen atoms in the diamine, two oxygen atoms in acac and two oxygen atoms in bidentate NO₃[−]. The weak IR absorption band with splitting in the region of 1700–1800 cm^{-1} is diagnostic for the coordination mode of NO₃[−]. When NO₃[−] is monodentate, the splitting is small ($\Delta\nu_{\text{NO}_3} = 20\text{--}25\text{ cm}^{-1}$), while bidentate NO₃[−] shows larger splitting.^{10,11} The IR data of complexes **1–5** in this region are given in Table 2. All the complexes show large splitting of this band ($\Delta\nu_{\text{NO}_3} = 45\text{--}51\text{ cm}^{-1}$), indicating that the NO₃[−] ion acts as a bidentate ligand.

Each of complexes **1** and **5** can exist as a pair of enantiomers (the Λ -form is drawn in Figure 1) although no X-ray crystal structure has been reported yet. For complexes with an asymmetrically substituted diamine, two diastereomers may be formed. In the present study, the structures of [Ni(EtMe₃en)(acac)(NO₃)] (**2**) and [Ni(*asym*-Et₂Me₂en)(acac)(NO₃)] (**3**) were determined by single-crystal X-ray diffraction methods. Complexes **2** and **3** are isomorphous (Table 1) and the molecular structures are also similar to each other. As shown in Figures 2 and 3, the nickel atom is coordinated with six donor atoms to form a distorted octahedron. The --NMe_2 group is trans to the oxygen atom in NO₃[−] while the --NEtMe or --NEt_2 group is trans to the oxygen atom in acac. The preferential formation of this isomer may be due to trans influence: a pair of the weaker donor (NO₃[−]) and the stronger donor (--NMe_2) are trans to each other and another pair of the stronger donor (acac) and the weaker donor (--NEtMe or --NEt_2) are also trans to each other.

**Figure 3.** ORTEP drawing of [Ni(*asym*-Et₂Me₂en)(acac)(NO₃)] (**3**). Displacement ellipsoids are drawn with 50% probability. H-atoms are excluded for clarity.**Table 3.** Selected Bond Lengths (Å) and Angles (°)

	2	3
Ni(1)–O(1)	2.021(3)	2.027(2)
Ni(1)–O(2)	1.986(3)	1.988(2)
Ni(1)–O(3)	2.116(3)	2.136(2)
Ni(1)–O(4)	2.194(3)	2.164(3)
Ni(1)–N(1)	2.093(4)	2.090(3)
Ni(1)–N(2)	2.186(3)	2.217(3)
N(3)–O(3)	1.265(4)	1.266(4)
N(3)–O(4)	1.253(5)	1.261(4)
N(3)–O(5)	1.225(4)	1.222(4)
O(1)–Ni(1)–O(2)	91.13(11)	91.47(9)
O(3)–Ni(1)–O(4)	59.57(13)	59.79(10)
N(1)–Ni(1)–N(2)	84.99(14)	84.74(11)
O(1)–Ni(1)–N(2)	178.07(11)	177.75(9)
O(2)–Ni(1)–O(3)	163.05(12)	162.96(11)
O(4)–Ni(1)–N(1)	157.44(13)	159.83(11)

In addition, the inter-ligand repulsion is smaller in this isomer than in the other diastereomer, because the more bulky --NEtMe or --NEt_2 group lies closer to the less bulky NO₃[−] rather than acac.

Selected bond lengths and angles are listed in Table 3. The bite angles of NO₃[−] are 59.6 and 59.8° in complexes **2** and **3**, respectively. Such a small bite angle is typical for bidentate nitrate⁴ and causes distortion from a regular octahedron. The terminal N(3)–O(5) bond in NO₃[−] is shorter than the other two N–O bonds because the coordination of an O atom causes elongation of the N–O bond involving this O atom, which in turn results in shortening of the neighboring N–O bond. The Ni(1)–N(2) bond (2.186(3) Å in **2** or 2.217(3) Å in **3**) is longer than Ni(1)–N(1) bond (2.093(4) Å in **2** or 2.090(3) Å in **3**). This difference in the bond length is attributed to steric hindrance of the ethyl group(s). The elongation is more significant for complex **3**, in which *asym*-Et₂Me₂en has two ethyl groups on one nitrogen atom. The trans influence also somewhat contributes to the difference in bond distance. In a similar complex with a bulky diamine [Ni(dipe)(acac)(NO₃)] (dipe = 1,2-dipiperidinoethane), the Ni–N bond distances [2.070(3) and 2.118(3) Å]² are similar to the Ni(1)–N(1) bond and shorter than the Ni(1)–N(2) bond. Although dipe has bulky piperidino groups, the alkyl moieties are bonded together and repulsion

Table 4. Absorption Maxima (10^3 cm^{-1}) and Molar Absorption Coefficients ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) of Complexes **1–5** in Various Solvents^{a)}

	Dichloroethane (DN ^{b)} = 0, AN ^{b)} = 17)	Acetone (DN = 17, AN = 13)	DMSO (DN = 30, AN = 19)	Nitromethane (DN = 2.7, AN = 21)
[Ni(Me ₄ en)(acac)(NO ₃)] (1)	9.56 (9.60) 16.29 (18.56)	9.57 (9.87) 16.26 (18.62)	9.44 (9.17) 15.80 (6.77)	9.60 (9.64) 16.29 (19.36)
[Ni(EtMe ₃ en)(acac)(NO ₃)] (2)	9.50 (9.42) 16.16 (18.69)	9.47 (9.34) 16.10 (18.12)	9.34 (8.12) 15.63 (6.20)	9.50 (9.32) 16.10 (19.28) 20.66 (5.44)
[Ni(<i>sym</i> -Et ₂ Me ₂ en)(acac)(NO ₃)] (3') ^{c)}	9.39 16.00	9.35 15.97	9.22 15.46	9.39 16.00 20.49
[Ni(<i>asym</i> -Et ₂ Me ₂ en)(acac)(NO ₃)] (3)	9.30 (9.33) 15.95 (19.30)	9.31 (9.04) 15.95 (18.20)	9.22 (7.32) 15.53 (6.08)	9.34 (8.51) 15.92 (18.30) 20.45 (10.11)
[Ni(Et ₃ Meen)(acac)(NO ₃)] (4)	9.23 (8.93) 15.87 (19.47)	9.19 (8.61) 15.82 (18.12)	9.08 (6.60) 15.29 (5.66)	9.22 (7.75) 15.80 (17.55) 20.28 (16.28)
[Ni(Et ₄ en)(acac)(NO ₃)] (5)	9.07 (8.72) 15.70 (19.65)	9.07 (8.67) 15.70 (18.67)	8.94 (6.00) 15.04 (6.20)	9.08 (7.16) 15.67 (16.49) 20.12 (25.01)

a) Concentration of the complex is $2.50 \times 10^{-2} \text{ mol dm}^{-3}$. b) DN denotes donor number and AN denotes acceptor number. See Ref. 5.

c) Accurate molar absorption coefficient could not be determined due to insufficient purity.

from the other part within the complex will be smaller than in the case of complexes **2** and **3**. As another example of asymmetric diamine, we have recently determined the crystal structure of analogous binuclear complex $[(\text{NO}_3)(\text{acac})\text{Ni}(\text{Me}_2\text{N-CH}_2\text{CH}_2\text{NMe})\text{CH}_2\text{CH}_2(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)\text{Ni}(\text{acac})(\text{NO}_3)]$.¹² In this complex, the Ni–N(MeCH₂CH₂) bonds are longer by ca. 0.1 Å than the Ni–NMe₂ bonds, similar to complex **2**.

Solution Equilibria of Complexes 1–5 in Various Solvents. Solvatochromic behaviors of complexes **1–5** have been examined in four solvents with different polarity, donor numbers, and acceptor numbers: 1,2-dichloroethane (DCE), acetone, dimethyl sulfoxide (DMSO), and nitromethane. The absorption peak positions and molar absorption coefficients are summarized in Table 4. Three different patterns were observed in the absorption spectra. As a representative example, the spectra of complex **3** are shown in Figure 4. The spectrum in DCE or acetone exhibits two absorption bands, and the intensity of the higher frequency band ($16.0 \times 10^3 \text{ cm}^{-1}$) is almost double of that of the lower one ($9.3 \times 10^3 \text{ cm}^{-1}$). This peculiar relationship is characteristic of octahedral nickel(II) complexes with a bidentate NO_3^- ,² suggesting that the complex is dissolved in DCE or acetone as $[\text{Ni}(\text{diam})(\text{acac})(\text{NO}_3)]$, the same structure as in the solid state. The electric conductivities were also measured for the same solutions in order to estimate the degree of dissociation to ions. As is seen in Table 5, the molar conductivities in DCE and acetone are quite low, which confirms that dissociation to ions is negligible. Since DCE and acetone have rather weak acceptor properties, the ion dissociation is not well promoted via solvation in these solvents.

Each of the absorption spectra of complexes **1–5** in DMSO also shows two absorption bands (see line c in Figure 4). The difference from the spectrum in DCE or acetone is the intensity ratio of the two bands. The intensity of the higher frequency band is almost the same as or slightly lower than that of the lower one in DMSO. This intensity ratio is normal for octahedral nickel(II) complexes with no bidentate NO_3^- . The

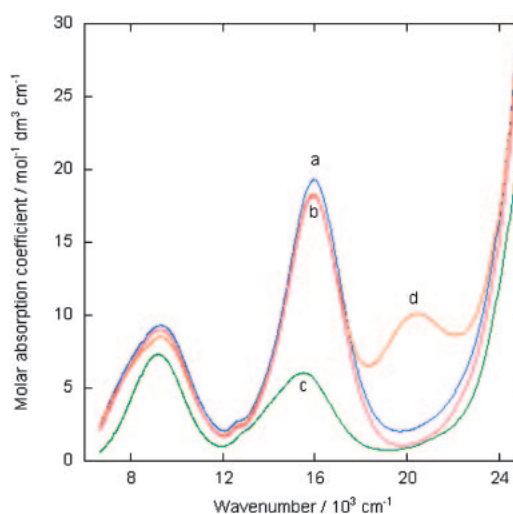
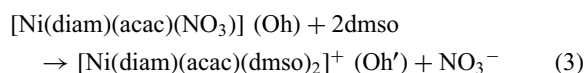


Figure 4. UV-vis spectra of $[\text{Ni}(\text{asym-Et}_2\text{Me}_2\text{en})(\text{acac})(\text{NO}_3)]$ (**3**) in (a) 1,2-dichloroethane, (b) acetone, (c) dimethyl sulfoxide, and (d) nitromethane.

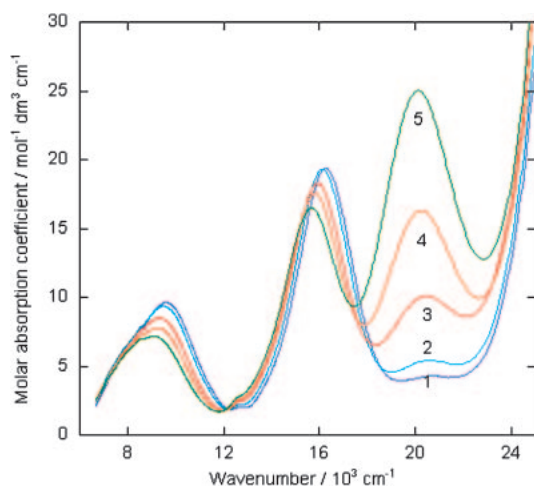
peak positions in DMSO are shifted to lower frequency as compared with those in DCE or acetone, suggesting that the species present in the DMSO solution is different from $[\text{Ni}(\text{diam})(\text{acac})(\text{NO}_3)]$. The molar conductivity of the DMSO solution corresponds to the value of an 1:1 electrolyte. These results indicate that $[\text{Ni}(\text{diam})(\text{acac})(\text{NO}_3)]$ completely dissociates into ions in DMSO at a concentration of $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ and the cationic complex is coordinated with two DMSO molecules forming another octahedral species as represented by eq 3.



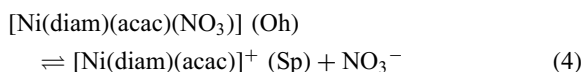
In nitromethane solution, the absorption spectrum showed a

Table 5. Molar Conductivity ($\text{S cm}^2 \text{mol}^{-1}$) at $25.0 \pm 0.1^\circ \text{C}^{\text{a}}$

	DCE	Acetone	DMSO	Nitromethane
$[\text{Ni}(\text{Me}_4\text{en})(\text{acac})(\text{NO}_3)]$ (1)	0.03	0.45	30.36	2.07
$[\text{Ni}(\text{EtMe}_3\text{en})(\text{acac})(\text{NO}_3)]$ (2)	0.06	1.66	31.12	4.34
$[\text{Ni}(\text{asym-Et}_2\text{Me}_2\text{en})(\text{acac})(\text{NO}_3)]$ (3)	0.09	1.72	31.04	5.64
$[\text{Ni}(\text{Et}_3\text{Meen})(\text{acac})(\text{NO}_3)]$ (4)	0.12	2.46	31.72	11.77
$[\text{Ni}(\text{Et}_4\text{en})(\text{acac})(\text{NO}_3)]$ (5)	0.23	1.47	28.33	15.65
Standard for an 1:1 electrolyte ^b	10–24	100–140	ca. 35	75–95

a) Concentration of the complex is $2.50 \times 10^{-2} \text{ mol dm}^{-3}$. b) Ref. 14.**Figure 5.** UV-vis spectra of $[\text{Ni}(\text{diam})(\text{acac})(\text{NO}_3)]$ in nitromethane at room temperature (1: Me_4en , 2: EtMe_3en , 3: $\text{asym-Et}_2\text{Me}_2\text{en}$, 4: Et_3Meen , 5: Et_4en).

new band at $(20.1\text{--}20.7) \times 10^3 \text{ cm}^{-1}$ in addition to the two bands that are similarly observed in DCE or acetone (see line d in Figure 4). This new band can be assigned to the d–d transition of the square-planar complex $[\text{Ni}(\text{diam})(\text{acac})]^+ \cdot \text{NO}_3^-$.^{1–4} The molar conductivities of complexes **1–5** in nitromethane are much lower than that of the standard 1:1 electrolyte but the non-negligible conductance indicates that some ionic species are formed in the solution. These results reveal that complexes **1–5** exist as an equilibrium mixture of the octahedral (Oh) and square-planar (Sp) forms as shown in eq 4.



A comparison of the absorbance at $(20.1\text{--}20.7) \times 10^3 \text{ cm}^{-1}$ (Figure 5) and the molar conductivity values (Table 5) shows that the dissociation constant increases in the order of diam; $\text{Me}_4\text{en} < \text{EtMe}_3\text{en} < \text{asym-Et}_2\text{Me}_2\text{en} < \text{Et}_3\text{Meen} < \text{Et}_4\text{en}$ in this series of complexes. The absorbance due to the Sp form for $\text{sym-Et}_2\text{Me}_2\text{en}$ complex **3'** is similar to that for $\text{asym-Et}_2\text{Me}_2\text{en}$ complex **3**, but quantitative discussion should be avoided due to the insufficient purity of complex **3'** (see Experimental). The above order of the dissociation constant is interpreted as follows: with increase of the bulkiness of the substituents in diam (i.e., increase in the number of ethyl groups), the relief of steric strain accompanying with the dissociation of NO_3^- becomes more significant, resulting in preference of the Sp form.

The substituents in the diamine also affect the ligand-field stabilization energy (LFSE) of the complexes. For an octahedral complex, the LFSE can be evaluated by the first d–d transition energy. As is seen in Table 4, the wavenumber of the lowest d–d transition in DCE or acetone decreases in the order of diam: $\text{Me}_4\text{en} > \text{EtMe}_3\text{en} > \text{sym-Et}_2\text{Me}_2\text{en} > \text{asym-Et}_2\text{Me}_2\text{en} > \text{Et}_3\text{Meen} > \text{Et}_4\text{en}$. The peak position of the first d–d transition band in DMSO is almost parallel to that in DCE. The observed order indicates that diam having more ethyl groups acts as a weaker donor although the electron-donating ability of ethyl group is higher than that of methyl group. This result can be explained by the decrease in LFSE due to steric hindrance caused by the ethyl groups, which is reflected in the Ni–N bond elongation. The two ethyl groups on the same nitrogen atom in $\text{asym-Et}_2\text{Me}_2\text{en}$ causes a larger steric effect than the ethyl groups on different nitrogen atoms in $\text{sym-Et}_2\text{Me}_2\text{en}$. As for the relationship between the ligand-field strength and the Sp–Oh equilibrium in Ni^{II} complexes, a ligand with higher LFSE generally more stabilizes the Sp form. In this series of complexes, however, the opposite tendency is observed. Although quantitative interpretation of this result is difficult, it seems that the difference in the LFSE is relatively small and that the equilibrium shown in eq 4 is predominantly determined by the steric effects. Interestingly, this trend does not hold for mixed-ligand complexes with diamines in which the conformation of substituents are restricted. For $[\text{Ni}(\text{dipe})(\text{acac})(\text{NO}_3)]$ and $[(\text{NO}_3)(\text{dipm})\text{Ni}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe})\text{CH}_2\text{CH}_2(\text{NMeCH}_2\text{CH}_2\text{NMe}_2)\text{Ni}(\text{dipm})(\text{NO}_3)]$ (dipm = dipivaloylmethanate), the dissociation constant is much lower than those of complexes **2–5** in nitromethane even at higher temperatures.^{2,13} The difference in motional freedom can affect the entropy change in the equilibrium shown in eq 4. For the diamine with less freedom, the lower entropy gain will make the dissociation less favorable.

In conclusion, the present study has revealed that the presence of bulky *N*-alkyl groups in diam decreases the ligand-field stabilization energy (LFSE) for a series of mixed-ligand complexes $[\text{Ni}(\text{Et}_x\text{Me}_{4-x}\text{en})(\text{acac})(\text{NO}_3)]$ ($x = 0\text{--}4$). These complexes partially liberate the nitrate ion in nitromethane solution, and the degree of dissociation increases with an increase of the number of ethyl groups, despite the lowered ligand-field strength.

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- # Dedicated to Professor Naomi Hoshino-Miyajima
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