

Synthesis and Characterization of Nickel(II) Schiff Base Complexes with Methoxy or Methyl Groups at 2,6-Positions of the Pendant Phenyl Ring: the Control of *cis* and *trans* Geometries

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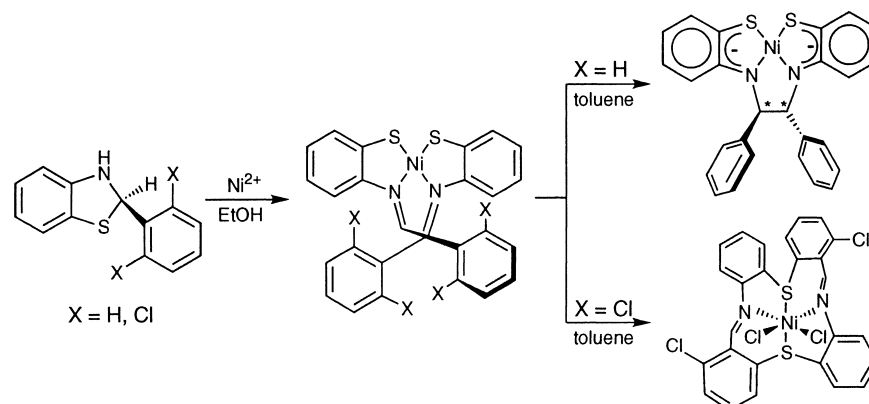
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Two nickel(II) complexes with N,S chelates were prepared by the reaction of nickel(II) acetate tetrahydrate with 2-substituted benzothiazolines. Bis[2-(2,6-dimethoxyphenyl)methyleneamino]benzenethiolato]nickel(II) **1**, in which the 2,6-positions of the pendant phenyl ring are occupied by methoxy groups, has an approximately square-planar geometry around a nickel atom with a *cis*-N₂S₂ donor atom arrangement. X-ray and variable-temperature ¹H NMR studies indicated the existence of an apical Ni⋯OMe interaction in **1**. On the other hand, bis[2-(mesitlmethyleneamino)benzenethiolato]nickel(II) **2** with methyl groups at the 2,4,6-positions of the pendant phenyl ring exhibits a perfect planar *trans*-N₂S₂ coordination around the nickel atom. An X-ray study revealed the existence of an intraligand CH/π interaction in **2**. A difference in the geometry around –CH=N– (*E* and *Z*) was also observed between **1** and **2** (*Z* for **1** and *E* for **2**).

It is well-known that 2-substituted benzothiazolines are suitable starting materials to yield Schiff base metal complexes with N,S chelates.^{1,2} In fact, a variety of nickel(II), palladium(II), and platinum(II) complexes containing Schiff base ligands with N,S donor atoms have been prepared by treating M(AcO)₂ with several 2-substituted benzothiazolines.^{3–6} One of the most interesting features of these Schiff base complexes is their reactivities, which are dependent on the central metal ion. For example, it has been found that square-planar palladium(II) and platinum(II) complexes derived from 2-(1-naphthyl)benzothiazoline are easily metallated at the *ortho*-position of the pendant 1-naphthyl ring to yield thiolato-bridged tetranuclear complexes,³ owing to C–H bond activation, which is well observed in N-donor ligands, such as Schiff bases and azo-derivatives.⁷ However, cyclometallation in the corresponding nickel(II) complexes has not yet been observed. In-

stead, we have found that a square-planar Schiff base nickel(II) complex with unsubstituted phenyl groups as a pendant arm is converted into a nickel(II) complex with a non-innocent ligand, of which the electric structure can not be described by a common structural formula (Scheme 1).⁴ In addition, a nickel(II) complex containing chlorine atoms at the 2,6-positions of the pendant phenyl ring was found to be converted into an octahedral nickel(II) complex with a macrocyclic ligand generated by the activation of C–Cl bonds (Scheme 1).⁵ Thus, the C(aryl)–R(substituent groups) bond activation in square-planar metal complexes as well as our general interest in metal complexes coordinated by mixed sulfur-nitrogen donor atoms promoted us to investigate the structure and properties of Schiff base nickel(II) complexes with substituent groups on the pendant phenyl ring. Herein we report on the synthesis and characterization of two nickel(II) complexes with the 2,6-disubsti-



Scheme 1.

tuted pendant phenyl rings by methoxy or methyl groups.

Experimental

General Procedures. All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. The reagents were commercial samples, and were not purified further.

Infrared spectra were obtained on a JASCO FT/IR-5000 Infrared Spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$) using the Nujol mulls, NMR spectra on a JEOL EX 270 instrument using tetramethylsilane as internal standard (δ 0) and UV/vis spectra on a JASCO V-570 spectrophotometer. Elemental analyses were performed at Osaka University.

Synthesis of 2-(2,6-Dimethoxyphenyl)benzothiazoline. 2-(2,6-Dimethoxyphenyl)benzothiazoline was prepared according to a literature procedure for 2-substituted benzothiazolines.⁸ To a solution of 2,6-dimethoxybenzaldehyde (0.25 g, 1.5 mmol) in ethanol (20 mL) was added 2-aminothiophenol (0.20 g, 1.6 mmol); the solution was then heated under reflux for 30 min. The resulting solution was allowed to cool in a refrigerator overnight. Pale yellow crystals were collected by filtration and dried in vacuo. Yield: 0.27 g, 66%. Found: C, 65.77; H, 5.59; N, 5.12%. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}$: C, 65.91; H, 5.53; N, 5.12%. IR (Nujol) $\nu_{\text{max}}/\text{cm}^{-1}$ 3310 (NH). ^1H NMR (270 MHz, CDCl_3 , r.t.) δ 7.24 (1H, t, J = 8.4 Hz, aryl CH), 7.14 (1H, d, J = 7.3 Hz, aryl CH), 6.97 (1H, s, 2-CH), 6.93 (1H, dd, J = 8.8 and 1.7 Hz, aryl CH), 6.84 (2H, t, J = 7.5 Hz, aryl CH), 6.57 (2H, d, J = 8.6 Hz, aryl CH), and 3.78 (6H, s, OCH_3).

Synthesis of Bis[2-(2,6-dimethoxyphenyl)methyleneamino]benzenethiolato]nickel(II) 1. 2-(2,6-Dimethoxyphenyl)benzothiazoline (0.23 g, 0.84 mmol) and nickel(II) acetate tetrahydrate (0.11 g, 0.44 mmol) were refluxed in ethanol (20 mL) for 1.5 h. Brown microcrystals precipitated upon cooling to room temperature were collected by filtration. Yield: 0.17 g, 64%. Crystals of complex **1** suitable for a structure determination were grown by the slow diffusion of diethyl ether into a CH_2Cl_2 solution of **1**. Found: C, 59.48; H, 4.77; N, 4.59%. Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NiO}_4\text{S}_2$: C, 59.72; H, 4.68; N, 4.64%. IR (Nujol) $\nu_{\text{max}}/\text{cm}^{-1}$ 1603 (C=N). ^1H NMR (270 MHz, CDCl_3 , -50°C) δ 7.86 (2H, s, CH=N), 7.42 (2H, t, J = 8.2 Hz, aryl CH), 7.33 (2H, d, J = 6.9 Hz, aryl CH), 6.94 (2H, t, J = 7.4 Hz, aryl CH), 6.68 (2H, t, J = 7.1 Hz, aryl CH), 6.52 (2H, d, J = 8.2 Hz, aryl CH), 6.32 (2H, d, J = 7.9 Hz, aryl CH), 6.30 (2H, d, J = 8.6 Hz, aryl CH), 3.96 (6H, s, OCH_3), and 3.79 (6H, s, OCH_3). UV-vis: (CHCl_3) $\sigma_{\text{max}}/10^3\text{ cm}^{-1}$ [$\log(\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1})$]: 16.0(sh) (2.59) and 22.2 (3.61).

Synthesis of Bis[2-(mesitylmethyleneamino)benzenethiolato]nickel(II) 2. A solution of mesitaldehyde (0.24 g, 1.62 mmol) and 2-aminothiophenol (0.21 g, 1.67 mmol) in ethanol (20 mL) was refluxed for 1 h. After the resulting solution was cooled to room temperature, nickel(II) acetate tetrahydrate (0.20 g, 0.80 mmol) was added [2-(mesit)benzothiazoline was not isolated]. The mixture was refluxed for 20 min and cooled to room temperature. Precipitated brown powder was collected by filtration and recrystallized from CHCl_3 . Yield: 0.25 g, 53%. Crystals of complex **2** suitable for a structure determination were grown by the slow diffusion of diethyl ether into a CHCl_3 solution of **2**. Found: C, 65.71; H, 5.55; N, 4.89%. Calcd for $\text{C}_{32}\text{H}_{32}\text{N}_2\text{NiS}_2\cdot 0.2\text{CHCl}_3$: C, 65.41; H, 5.49; N, 4.74%. IR (Nujol) $\nu_{\text{max}}/\text{cm}^{-1}$ 1597 (C=N). ^1H NMR (270 MHz, CDCl_3 , r.t.) δ 9.19 (2H, s, CH=N), 7.33 (2H, dd, J = 7.8 and 1.2 Hz, aryl CH), 6.85 (2H, t, J = 7.6 Hz, aryl CH), 6.75 (4H, s, aryl CH), 6.32 (2H, t, J = 7.8 Hz, aryl CH), 6.02

(2H, d, J = 7.9 Hz, aryl CH), 2.24 (6H, s, CH_3), and 2.00 (12H, s, CH_3). UV-vis: (CHCl_3) $\sigma_{\text{max}}/10^3\text{ cm}^{-1}$ [$\log(\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1})$]: 14.1 (2.06) and 21.2 (3.41).

Thermal Reaction of 1 and 2 in Toluene. Suspensions of **1** (0.123 g) and **2** (0.094 g) in toluene (30 mL) were refluxed for 1.5 and 3 h, respectively, and the resulting solutions, which showed one spot in TLC, were cooled to room temperature. The resulting precipitates (0.099 g for **1** and 0.041 g for **2**) were collected by filtration, and analyzed by ^1H NMR, showing **1** and **2**.

X-ray Crystallography. X-ray measurements of complexes **1** and **2** were made on a Mac Science MXC3 diffractometer with Mo $K\alpha$ radiation (λ = 0.71073 Å) at room temperature. θ - 2θ scans were employed and empirical absorption corrections (ψ scans) were applied. The solution and refinement procedures were made by applying the CRYSTAN-GM package.⁹ The structures of complexes **1** and **2** were solved by direct methods using PATTY in DIRDIF¹⁰ and SIR 92,¹¹ respectively, and refined anisotropically for all non-hydrogen atoms with full-matrix least-squares calculations. All hydrogen atoms for **1** were calculated with a C-H distance of 0.96 Å and refined isotropically. Hydrogen atoms for **2** were generated by difference Fourier synthesis, except for the hydrogen atoms (H31A,B,C and H32A,B,C) for two methyl groups which were located at the computed positions; all hydrogen atoms were refined isotropically. Crystallographic data for **1** and **2** are given in Table 1. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 186593 and 186594.

Results and Discussion

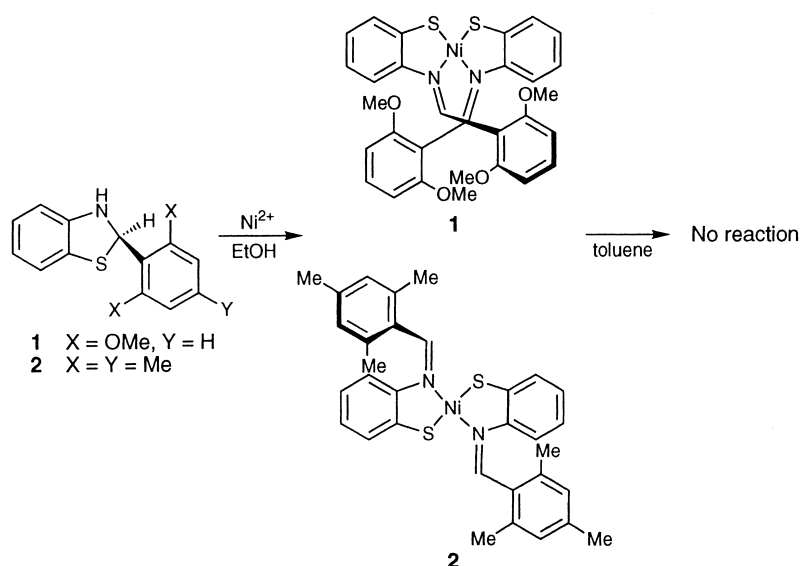
Syntheses and Properties. 2-(2,6-Dimethoxyphenyl)benzothiazoline was prepared by a reaction of 2-aminothiophenol with 2,6-dimethoxybenzaldehyde in ethanol. This compound was isolated as pale yellow crystals, and characterized by IR and NMR spectroscopies, besides elemental analysis. Because 2-(mesit)benzothiazoline, which was prepared from 2-aminothiophenol and mesitaldehyde, is a liquid at room temperature, it was used for the reaction without isolation. The reactions of nickel(II) acetate tetrahydrate with 2-(2,6-dimethoxyphenyl)benzothiazoline or 2-(mesit)benzothiazoline proceeded smoothly in ethanol to produce **1** and **2** (Scheme 2), which were determined by X-ray analyses to be bis(bidentate-N,S)-type square-planar nickel(II) complexes, *cis*-isomer for **1** and *trans*-isomer for **2** (vide infra). Complexes **1** and **2** are fairly stable in solution, and no subsequent reaction occurred even after refluxing for a few hours in toluene. This is in contrast to the case of a nickel(II) complex with unsubstituted phenyl groups as a pendant arm, which is converted into a nickel(II) complex with a non-innocent ligand through carbon-carbon bond formation (Scheme 1).⁴ In addition, the activation of C(aromatic)- OCH_3 or C(aromatic)- CH_3 bonds was also not recognized for **1** and **2**, while it has been shown that heating the nickel(II) complex with chlorine atoms at 2,6-positions of the pendant phenyl ring in toluene gives a distorted octahedral nickel(II) complex by C(aromatic)-Cl bond activation (Scheme 1).⁵ The stability of **2** can be explained by the *trans* arrangement, which prevents contact of the two azomethine groups required for carbon-carbon bond formation, besides the contact between the metal center and the methyl carbon

Table 1. Crystallographic Data for **1** and **2** Complexes

	1	2
Formula	C ₃₀ H ₂₈ N ₂ NiO ₄ S ₂ ·CH ₂ Cl ₂	C ₃₂ H ₃₂ N ₂ NiS ₂
<i>M</i>	688.32	567.44
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	13.598(6)	10.21(1)
<i>b</i> /Å	21.225(9)	14.738(9)
<i>c</i> /Å	11.056(5)	9.80(1)
α /°		90.92(7)
β /°	99.79(4)	103.30(8)
γ /°		100.49(6)
<i>V</i> /Å ³	3144(2)	1409(2)
<i>Z</i>	4	2
μ /mm ⁻¹	0.955	0.856
No. unique reflections measured	4490	5496
No. reflections in refinement	2780 (<i>I</i> > 2.0 σ (<i>I</i>))	4551 (<i>I</i> > 2.0 σ (<i>I</i>))
<i>R</i>	0.063	0.056
<i>R</i> _w	0.062	0.062

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2},$$

Weighting scheme: $1/[\sigma^2(F_o) + 0.001F_o^2]$.



Scheme 2.

atom for the activation of C(aromatic)–CH₃ bond. On the other hand, **1** is possibly stabilized by the existence of the apical Ni···OMe interaction, as evidenced by an X-ray analysis, which would prevent any further reaction.

The electronic spectra of **1** and **2** in the visible region consist of two absorption components (Fig. 1). The weak band at lower energy (ca. $15 \times 10^3 \text{ cm}^{-1}$) and the intense band at higher energy (ca. $20 \times 10^3 \text{ cm}^{-1}$) for each complex are assigned as a ligand field (LF) and ligand-to-metal charge transfer (LMCT) transitions, respectively.¹² The LF transition for **2**, which has a *trans* coordination geometry, occurs as a well-defined band at $14.1 \times 10^3 \text{ cm}^{-1}$, while the absorption spectrum of **1**, having a *cis* geometry, gives a LF transition shoulder at a higher energy of $16.0 \times 10^3 \text{ cm}^{-1}$. Because similar absorption shoulders due to LF transitions have been commonly

recognized for the related *cis*-N₂S₂ type nickel(II) complexes,^{4,5} this spectral feature may be used for the discrimination of *cis* and *trans* isomers.

In the ¹H NMR spectrum at 25 °C in CDCl₃, **1** exhibited one broad resonance for *ortho*-methoxy groups (Fig. 2). As the temperature was lowered from 25 to –50 °C, however, this resonance became two separate signals (δ 3.79 and 3.96 at –50 °C), one of which is located considerably downfield of δ 3.96 compared with the corresponding signal for 2-(2,6-dimethoxyphenyl)benzothiazoline (δ 3.78). Furthermore, the spectrum of **1** at –50 °C gave two doublets centered at δ 6.30 and 6.52 due to inequivalent *meta* protons of the pendant phenyl ring,¹³ which appeared as a broad signal at 25 °C. Thus, it is assumed that the rotation about the CH–C₆H₃(OMe)₂ moiety of **1**, which occurs on the NMR time scale at room tempera-

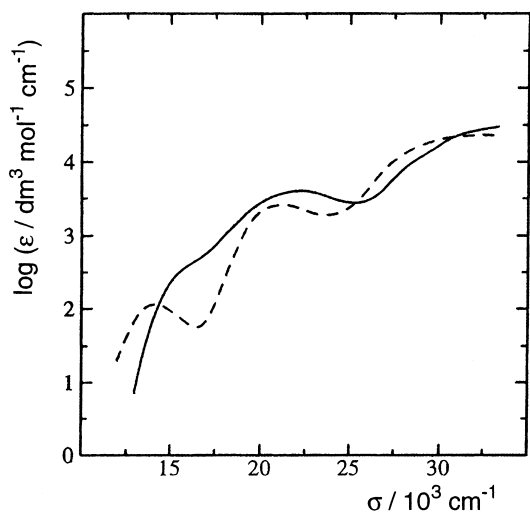


Fig. 1. Electronic absorption spectra of **1** (solid line) and **2** (broken line) in CHCl_3 .

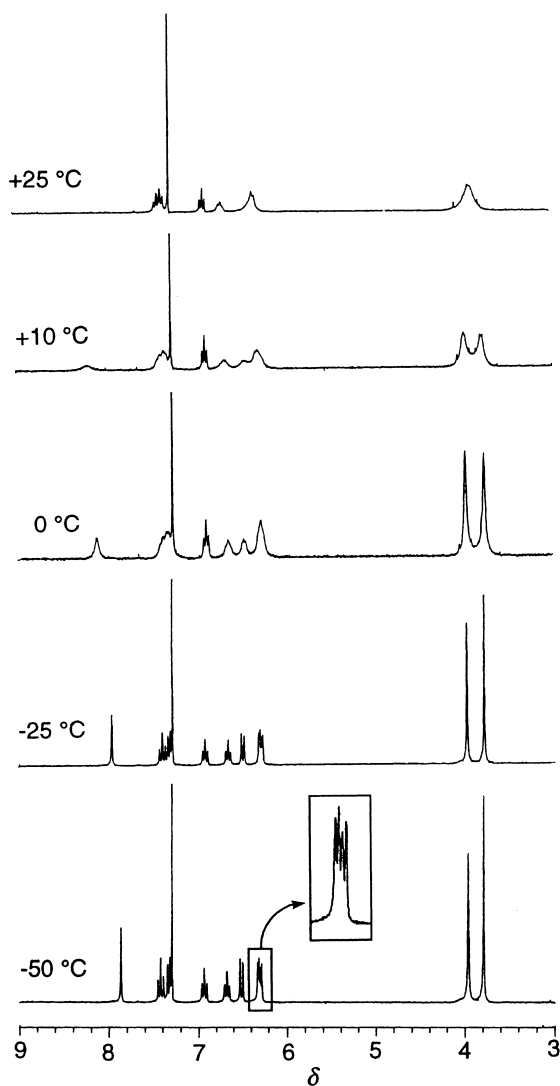


Fig. 2. Variable-temperature ^1H NMR spectra of **1** in CDCl_3 from +25 °C to -50 °C.

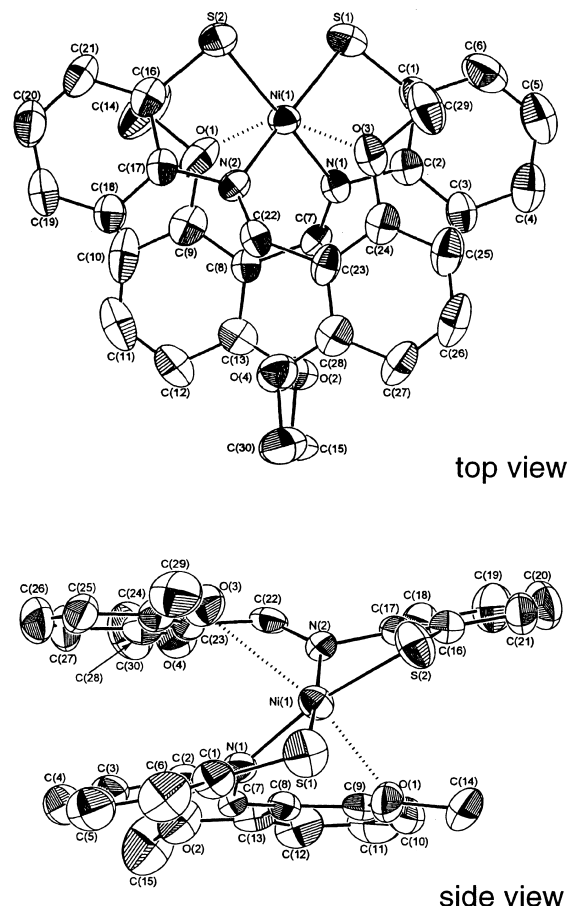


Fig. 3. Molecular structure of **1** with 50% probability ellipsoids. H atoms and the included solvent molecule are omitted for clarity.

ture, is restricted at low temperature in solution, because of the existence of the intramolecular $\text{Ni}\cdots\text{OMe}$ interaction.¹⁴ Contrary to the broad resonances for **1** at 25 °C, sharp resonances were observed in the ^1H NMR spectrum of **2** at room temperature: one singlet at δ 9.19 due to azomethine protons, four signals at δ 6.02, 6.32, 6.85, and 7.33 due to 2-iminothiophenol moieties, one singlet at δ 6.75 due to pendant phenyl rings, and two singlets at δ 2.00 and 2.24 with intensities 12H:6H due to methyl groups. These signals for **2** correspond to a half-set of protons, consistent with the C_2 -symmetrical structure. It is noteworthy that the azomethine signal for **2** shows a significant downfield shift (δ 9.19) compared with that for **1** (δ 7.86 at -50 °C). This downfield shift for **2** may be related to the intramolecular $\text{C}-\text{H}\cdots\text{S}$ interaction due to the short contact between the azomethine proton and the coordinated sulfur atom of the other chelate.¹⁵

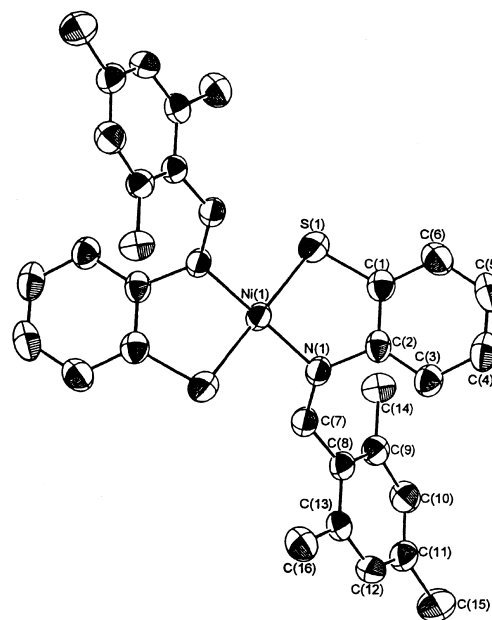
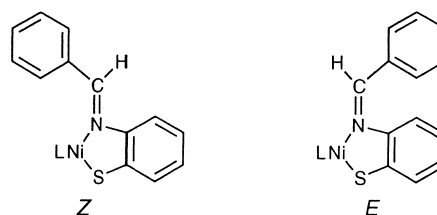
Molecular Structure of Complex 1. The molecular structure of **1**, together with the atomic labeling scheme, is shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. Complex $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$ crystallizes in the monoclinic space group $P2_1/a$. The asymmetric unit of $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$ consists of one nickel center and one dichloromethane. The coordination geometry around the nickel atom is an approximately square-planar, having a *cis*- N_2S_2 coordination mode. The dihedral angle between the two $\text{S}-\text{Ni}-\text{N}$ planes is $12(3)^\circ$. The

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1** and **2** Complexes

	1	2
Ni1–S1	2.184(4)	2.204(13)
Ni1–S2	2.172(4)	
Ni1–N1	1.913(9)	1.893(12)
Ni1–N2	1.928(9)	
Ni2–S2		2.198(2)
Ni2–N2		1.900(3)
S1–C1	1.754(13)	1.747(4)
S2–C16	1.763(13)	
S2–C17		1.754(4)
N1–C2	1.450(15)	1.446(5)
N1–C7	1.278(14)	1.292(5)
N2–C17	1.444(15)	
N2–C22	1.281(15)	
N2–C18		1.437(4)
N2–C23		1.283(5)
S1–Ni1–S2	90.2(2)	
S1–Ni1–N1	87.2(3)	86.5(5)
S1–Ni1–N1*		93.5(6)
S2–Ni1–N2	87.4(3)	
N1–Ni1–N2	96.3(4)	
S2–Ni2–N2		85.2(1)
S2–Ni2–N2*		94.8(1)

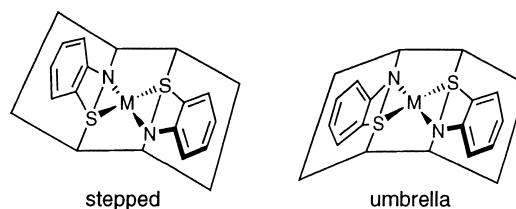
Ni–S (average 2.178 Å) and Ni–N (average 1.921 Å) bond distances are quite normal.^{2,4,5} Axial intramolecular Ni...OMe contacts of 2.630(9) Å for Ni(1)...O(1) and 2.709(9) Å for Ni(1)...O(3) in **1** should be noted. These contacts are significantly shorter than the sum of their van der Waals distances (3.15 Å).¹⁶ A similar interaction has been observed between the metal center and the methoxy-oxygen atom for nickel(II) or palladium(II) complexes with aromatic phosphines.¹⁷ The oxygen atoms of the methoxy groups may therefore be considered to coordinate weakly to the nickel atom, or at least to have an attractive interaction with the nickel one.¹⁸

Molecular Structure of Complex 2. The molecular structure of **2**, together with the atomic labeling scheme, is shown in Fig. 4. Selected bond lengths and angles are listed in Table 2. Complex **2** crystallizes in the triclinic space group $P\bar{1}$. There are two crystallographically independent molecules of **2** in the asymmetric unit which are almost the same as each other. Each molecule lies on an inversion center, the two Ni atoms being situated at (0, 0, 0) and (0.5, 0.5, 0.5). Thus, **2** adopts a perfect planar geometry around the nickel atom with a *trans*-N₂S₂ donor atom arrangement. A rough consideration based on molecular models suggests that the *trans* isomer was formed preferentially due to a less severe steric repulsion among the methyl groups of the pendant arms and the Ni center. Such a *trans* coordination geometry is unusual for bis-chelate N₂S₂ metal complexes with Schiff base ligands.¹⁹ The only example of a *trans* isomer for N₂S₂ Schiff base complexes derived from 2-substituted benzethiazolines is *trans*-[Pt(fabt)₂] (fabt = 2-(ferrocenylmethyleneamino)benzenethiolato) containing ferrocenyl groups as a pendant arm.⁶ However, a marked difference in another geometrical isomerism (*E* or *Z*) due to the restricted –C=N– double bond (Scheme 3)²⁰ is ob-

Fig. 4. One of the crystallographically independent molecules of **2** with 50% probability ellipsoids. H atoms are omitted for clarity.

Scheme 3.

served between **2** and *trans*-[Pt(fabt)₂]. That is, **2** has an *E* geometry about the C=N double bond, while the pendant arms of *trans*-[Pt(fabt)₂] is restricted to have a *Z* geometry. In addition, **2** adopts a stepped conformation with respect to the metal-containing 2-iminothiophenol moieties, which is different from an umbrella conformation for *trans*-[Pt(fabt)₂] (Scheme 4).⁶ In **2**, the Ni–S bond distances (average 2.201 Å) are longer, while the Ni–N bond distances (average 1.897 Å) are in the shorter region, compared with the values found in the related square-planar nickel(II) complexes having a *cis*-N₂S₂ coordination mode.^{2,4,5} This would be a reflection of the mutual *trans* influence due to coordinated sulfur atoms. The azomethine hydrogen atoms and the coordinated sulfur atoms show short contacts of C(7)–H(7)...S(1)* 2.48(4) and C(23)–H(23)...S(2)* 2.55(3) Å, accompanying the *E* geometry about C=N double



Scheme 4.

bond in **2**. Furthermore, it should be noted that the methyl groups of the pendant phenyl rings contact with 2-iminothiophenol moieties (C(2)···C(14) 3.079(6) and C(18)···C(30) 3.105(6) Å), indicative of the existence of an intraligand CH/π interaction.²¹ As a result, the pendant phenyl rings approach to the 2-iminothiophenol moieties having tilting angles of 58(3)° for Ni(1) and 58(4)° for Ni(2) between the pendant phenyl rings and the 2-iminothiophenol moieties.

Conclusion

We have synthesized and characterized two Schiff base nickel(II) complexes with different substituents on the pendant phenyl ring. The nickel(II) complex bearing the methoxy groups at the 2,6-positions of the pendant phenyl ring (**1**) shows an approximately square-planar geometry with a *cis*-N₂S₂ donor atom arrangement. The existence of the apical Ni···OMe interaction in the *cis* complex **1** has been established based on an X-ray analysis, together with variable-temperature ¹H NMR studies. On the other hand, the nickel(II) complex with methyl groups as a substituent group (**2**) exhibits a perfect planar *trans*-N₂S₂ coordination. These results suggest that the geometry of nickel(II) complexes of this type is successfully controlled by changing the substituent on the pendant phenyl ring. In addition, no further reactivity has been observed for both complexes, which is ascribed to the existence of the apical Ni···OMe interaction for **1** and to the *trans* arrangement for **2**. We are currently investigating the structure and reactivity of other metal complexes containing the same ligands employed in this work.

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