DALTON
FULL PAPER

CH/π interaction in nickel(II) complexes derived from 2-substituted benzothiazolines

Tatsuya Kawamoto * **and Yoshihiko Kushi**

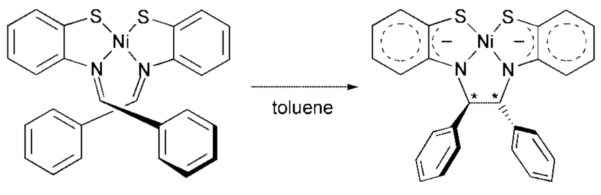
Department of Chemistry, Graduate School of Science, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560-0043, Japan. E-mail: kaw@ch.wani.osaka-u.ac.jp

Received 6th April 2000, Accepted 14th July 2000
Published on the Web 8th August 2000

By reaction of 2-(3,5-di-*tert*-butyl-4-hydoxyphenyl)benzothiazoline with nickel(II) acetate tetrahydrate, the complex bis[2-(3,5-di-*tert*-butyl-4-hydroxyphenylmethyleneamino)benzenethiolato]nickel(II) **1** has been prepared. Its crystal structure has been elucidated, showing an intramolecular approach of the *tert*-butyl group to the aromatic ring of the 2-aminobenzenethiol moiety. In addition, variable-temperature ^{1}H NMR studies of **1** indicated the restriction of rotation of the pendant arm. Such behaviour is attributed to the existence of a CH/π interaction between the *tert*-butyl group and the aromatic ring of another ligand. To provide further evidence for the CH/π interaction in nickel(II) complexes derived from 2-substituted benzothiazolines, we have also prepared a pair of nickel(II) complexes (**2** and **3**) with *meta*-substituted phenyl groups as pendant arms. A comparison between **2** with a methyl group and **3** with a chlorine atom on the pendant arm provided insight into the CH/π interaction that controls the orientation of the pendant arm.

Introduction

2-Substituted benzothiazolines for several metal ions act as Schiff base ligands with N,S donor atoms.[1] Indeed, we have reported that the reactions of a variety of metal ions with 2-substituted benzothiazolines gave the corresponding Schiff base metal complexes.[2] Furthermore, we have demonstrated that the formation of a carbon–carbon bond in the nickel(II) complex derived from 2-phenylbenzothiazoline took place, yielding a complex with a non-innocent ligand, even at room temperature (Scheme 1).[3] Our most recent contribution to this area is the demonstration that the arrangement around the metal centre is likely to be controlled by the steric effect of the pendant arm of the ligand as well as by the properties of the metal centre; in the case of the nickel(II) and palladium(II) complexes with phenyl or 1-naphthyl groups as pendant arms only *cis* isomers were formed,[3,4] but the platinum(II) complex with a ferrocenyl group was obtained as the *trans* and *cis* isomeric pair.[5] We expected that introduction of the *tert*-butyl group as a bulky substituent would improve the possibilities of studying the influence of ligand modifications on the properties of metal complexes.



Scheme 1

In the present paper we describe the chemical properties of nickel(II) complex obtained starting from 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzothiazoline. Through an examination of the nickel(II) complex with a *tert*-butyl group and a pair of nickel(II) complexes with *meta*-substituted phenyl groups as pendant arms, the work herein allows us to assess the significance of CH/π interactions in altering the reactivity of the metal complex and the orientation of the pendant arm.

Experimental

General

All reactions were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. Reagents were commercial samples and not purified further.

Infrared spectra were obtained on a Perkin-Elmer 983G Infrared Spectrophotometer (4000–180 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 Hitachi U-3400 spectrophotometer. Elemental analyses were performed at Osaka University.

Syntheses

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)benzothiazoline. 2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)benzothiazoline was prepared according to a literature procedure for 2-substituted benzothiazolines.[6] 2-Aminobenzenethiol (1.31 g, 10.5 mmol) and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (2.50 g, 10.3 mmol) in ethanol (20 cm^3) were refluxed for 20 min. The resulting solution was reduced to approximately one half of the initial volume under reduced pressure and allowed to cool in a refrigerator overnight. The light yellow crystals were filtered off and dried *in vacuo*. Yield 1.64 g, 47% (Found: C, 73.51; H, 7.99; N, 4.09. $C_{21}H_{27}NOS$ requires C, 73.85; H, 7.97; N, 4.10%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 3624s (OH), 3307m (NH) and 1574s (aromatic C=C); δ_H(270 MHz, CDCl$_3$) 7.40 (2 H, s, benzene), 7.05 (1 H, dd, $J = 7.6$ and 1.0, benzene), 6.94 (1 H, dd, $J = 7.7$ and 1.2, benzene), 6.75 (1 H, dt, $J = 7.6$ and 1.0, benzene), 6.64 (1 H, dd, $J = 7.6$ and 0.7 Hz, benzene), 6.38 (1 H, s, 2-CH), 5.29 (1 H, s, OH) and 1.43 (18 H, s, *tert*-butyl); δ_C(67.8 MHz, CDCl$_3$) 154.0, 146.2, 135.8, 130.9, 127.2, 125.1, 123.6, 121.5, 120.4, 109.6, 71.4, 34.3 and 30.1.

Bis[2-(3,5-di-*tert*-butyl-4-hydroxyphenylmethyleneamino)-benzenethiolato]nickel(II) 1. 2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)benzothiazoline (0.39 g, 1.1 mmol) and nickel(II) acetate tetrahydrate (0.14 g, 0.56 mmol) were refluxed in ethanol (20 cm^3) for 30 min. On standing the reaction mixture overnight, a

J. Chem. Soc., Dalton Trans., 2000, 3022–3026 DOI: 10.1039/b002745f

brown powder was formed and collected by filtration. The brown product was recrystallized from $CHCl_3$–*n*-hexane. Yield 0.24 g, 55%. Crystals of complex **1** suitable for a structure determination were grown by slow diffusion of diethyl ether into a $CHCl_3$ solution of the brown product (Found: C, 65.61; H, 6.84; N, 3.67. $C_{42}H_{52}N_2NiO_2S_2\cdot0.25CHCl_3$ requires C, 65.94; H, 6.84; N, 3.64%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 3606m (OH) and 1596s, 1572m and 1560w (C=N and aromatic C=C); δ_H(270 MHz, $CDCl_3$) 7.80 (2 H, s, CH=N), 7.30 (2 H, dd, J = 7.9 and 1.0, benzene), 6.90 (2 H, t, J = 7.3, benzene), 6.58 (2 H, dt, J = 7.7 and 1.1, benzene), 6.30 (2 H, d, J = 7.9 Hz, benzene), 5.65 (2 H, s, OH) and 1.40 (36 H, s, *tert*-butyl); δ_C(67.8 MHz, $CDCl_3$) 167.9, 157.0, 150.3, 146.6, 136.9, 128.9, 128.4, 127.6, 126.9 (br), 121.4, 114.7, 34.5 and 30.2.

2-(*m*-Toluyl)benzothiazoline. 2-(*m*-Toluyl)benzothiazoline was prepared according to a literature procedure for 2-substituted benzothiazolines.[6] 2-Aminobenzenethiol (1.25 g, 9.99 mmol) and *m*-tolualdehyde (1.20 g, 9.99 mmol) in ethanol (20 cm^3) were refluxed for 1 h. The resulting solution was reduced to approximately one half of the initial volume under reduced pressure and allowed to cool in a refrigerator overnight. The light yellow crystals were filtered off and dried *in vacuo*. Yield 2.07 g, 91% (Found: C, 73.65; H, 5.83; N, 6.22. $C_{14}H_{13}NS$ requires C, 73.97; H, 5.76; N, 6.16%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 3380m (NH) and 1576s (aromatic C=C); δ_H(270 MHz, $CDCl_3$) 7.37 (1 H, s, benzene), 7.33 (1 H, d, J = 7.6, benzene), 7.24 (1 H, t, J = 7.6, benzene), 7.14 (1 H, d, J = 7.3, benzene), 7.04 (1 H, dd, J = 7.6 and 1.0, benzene), 6.95 (1 H, dt, J = 7.8 and 1.3, benzene), 6.76 (1 H, dt, J = 7.5 and 1.2, benzene), 6.66 (1 H, dd, J = 7.9 and 1.0 Hz, benzene), 6.36 (1 H, s, 2-CH), 4.33 (1 H, s, NH) and 2.35 (3 H, s, CH_3); δ_C(67.8 MHz, $CDCl_3$) 146.2, 141.3, 138.4, 129.4, 128.5, 127.1, 126.5, 125.3, 123.5, 121.5, 120.5, 109.6, 70.0 and 21.5.

Bis[2-(*m*-toluylmethyleneamino)benzenethiolato]nickel(II) 2. 2-(*m*-Toluyl)benzothiazoline (0.34 g, 1.5 mmol) and nickel(II) acetate tetrahydrate (0.19 g, 0.75 mmol) were refluxed in ethanol (20 cm^3) for 20 min. A brown powder of the product precipitated upon cooling to room temperature and was isolated by filtration. Yield 0.30 g, 78%. Crystals of complex **2** suitable for a structure determination were grown by slow diffusion of diethyl ether into a $CHCl_3$ solution of the brown product (Found: C, 65.69; H, 4.85; N, 5.56. $C_{28}H_{24}N_2NiS_2$ requires C, 65.77; H, 4.73; N, 5.48%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1590m and 1570m (C=N and aromatic C=C); δ_H(270 MHz, $CDCl_3$) 9.60 (2 H, s, benzene), 7.75 (2 H, s, CH=N), 7.59 (2 H, d, J = 6.9, benzene), 7.40 (2 H, dd, J = 7.8 and 1.2, benzene), 7.17–7.24 (4 H, m, benzene), 7.00 (2 H, dt, J = 7.4 and 1.2, benzene), 6.69 (2 H, dt, J = 7.6 and 1.3, benzene), 6.24 (2 H, d, J = 7.6 Hz, benzene) and 1.93 (6 H, s, Me); δ_C(67.8 MHz, $CDCl_3$) 166.6, 149.9, 146.8, 140.0, 134.8, 132.1, 130.6, 128.8, 128.7, 128.2, 126.4, 121.4, 116.3 and 20.6.

Bis[2-(3-chlorophenylmethyleneamino)benzenethiolato]nickel(II) 3. 2-Aminobenzenethiol (0.47 g, 3.8 mmol) was added to an ethanolic solution (30 cm^3) containing 3-chlorobenzaldehyde (0.53 g, 3.8 mmol). The mixture was refluxed for 1 h and then nickel(II) acetate tetrahydrate (0.46 g, 1.9 mmol) was added [2-(3-chlorophenyl)benzothiazoline was not isolated because it is a liquid at room temperature]. The mixture was refluxed for 20 min and then cooled to room temperature. The red-brown precipitate was isolated by filtration and dried *in vacuo*. Yield 0.81 g, 79%. (Found: C, 56.39; H, 3.42; N, 5.18. $C_{26}H_{18}Cl_2N_2NiS_2$ requires C, 56.55; H, 3.29; N, 5.08%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1592s, 1570m and 1552w (C=N and aromatic C=C); δ_H(270 MHz, $CDCl_3$) 8.86 (2 H, d, J = 7.3, benzene), 8.62 (2 H, s, benzene), 7.82 (2 H, s, CH=N), 7.36–7.43 (4 H, m, benzene), 7.15 (2 H, t, J = 7.9, benzene), 7.06 (2 H, t, J = 6.9, benzene), 6.73 (2 H, t, J = 7.6, benzene) and 6.30 (2 H, d, J = 7.9 Hz, benzene); δ_C(67.8 MHz, DMSO-d_6, using the solvent resonances as the internal reference standard) 168.1, 149.0, 145.2, 136.4, 134.0, 130.7, 130.1, 128.7, 128.6, 127.9, 127.5, 121.5 and 117.3.

Table 1 Crystallographic data for complexes **1** and **2**

	1	**2**
Formula	$C_{42}H_{52}N_2NiO_2S_2$	$C_{28}H_{24}N_2NiS_2$
M	739.71	511.30
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	12.724(7)	12.163(5)
b/Å	21.161(10)	14.804(5)
c/Å	15.295(11)	7.028(6)
α/°		90.06(5)
β/°	108.70(5)	106.80(5)
γ/°		86.29(3)
V/Å^3	3901(4)	1209(1)
Z	4	2
μ/mm^{-1}	0.637	0.989
No. unique reflections measured	1905	4654
No. reflections in refinement	1482 ($I > 1.5\sigma(I)$)	3826 ($I > 2.0\sigma(I)$)
R	0.068	0.085
R'	0.065	0.098

X-Ray crystallography

X-Ray crystallographic data were collected on a Mac Science MXC3 diffractometer with Mo-Kα (λ = 0.71073 Å) radiation at room temperature. θ–2θ scans were employed; no significant decomposition of the crystal occurred during the data collection. The solution and refinement procedures made use of the CRYSTAN-GM software package.[7] The structures of complexes **1** and **2** were solved by direct methods using SIR 92[8] and refined anisotropically for all non-hydrogen atoms with full-matrix least-squares calculations. Hydrogen atoms were calculated with a C–H distance of 0.96 Å and refined isotropically. Crystallographic data for **1** and **2** are listed in Table 1.

CCDC reference number 186/2091.

See http://www.rsc.org/suppdata/dt/b0/b002745f/ for crystallographic files in .cif format.

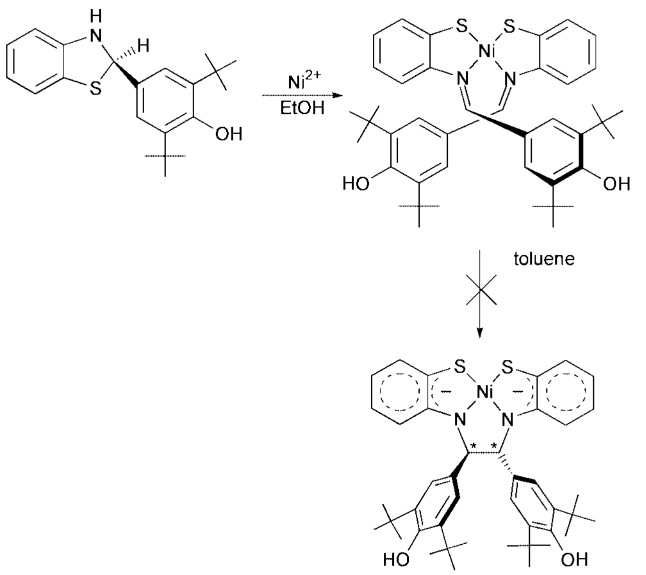
Results and discussion

The nickel(II) complex **1** was prepared from the 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzothiazoline and nickel(II) acetate tetrahydrate (Scheme 2). The IR spectrum shows the absence of ν(NH) vibration and the presence of multiplets of ν(C=N) and ν(aromatic C=C) vibrations near 1600 cm^{-1} as observed for nickel(II) complexes derived from 2-substituted benzothiazolines previously studied.[2–5] This indicates that the complex contains the ligand in Schiff base form. However, a part of the resonances due to the pendant arm of **1** were not observed in the ^{1}H NMR spectrum at room temperature. Furthermore, in an attempt to synthesize a nickel complex with a non-innocent ligand through carbon–carbon bond formation, a toluene solution of complex **1** was stirred, but no reaction occurred, even at higher temperature. This is in contrast to the behaviour of the nickel(II) complex with non-substituted phenyl group as pendant arm in Scheme 1.[3]

To determine unambiguously the structure of complex **1** an X-ray crystallographic study was undertaken. The molecular structure together with the atomic labeling scheme is shown in Fig. 1. In the molecule the metal atom lies on a crystallographic 2-fold axis. Selected bond distances and angles for **1** are given in Table 2. Though strong interligand steric interactions occur, the complex has a slightly distorted square planar geometry in

Table 2 Selected bond distances (Å) and angles (°) of complexes **1** and **2**

	1	**2**
Ni1–S1	2.163(8)	2.182(2)
Ni1–S2		2.184(2)
Ni1–N1	1.928(19)	1.925(5)
Ni1–N2		1.912(5)
S1–C1	1.76(3)	1.762(7)
S2–C21		1.761(7)
N1–C2	1.43(4)	1.427(8)
N1–C7	1.28(3)	1.296(8)
N2–C14		1.286(8)
N2–C22		1.431(8)
S1–Ni1–S1*	89.7(4)	
S1–Ni1–S2		93.9(1)
S1–Ni1–N1	87.5(6)	87.5(2)
S2–Ni1–N2		87.0(2)
N1–Ni1–N1*	95.8(9)	
N1–Ni1–N2		96.0(2)
Dihedral angle between NiNS planes	8(4)	23(3)



Scheme 2

which the nitrogen and sulfur donor atoms are *cis* to each other. The dihedral angle between the S–Ni–N planes is 8(4)°. The steric repulsion between ligands is decreased by a stepped conformation (Fig. 1(b)). Consequently, **1** shows a molecular helicity like analogous nickel(II) complexes. The bond parameters around the nickel atom are within the normal values.[2–5]

The steric bulk of the ligand through the *tert*-butyl group did not provide new significant information regarding the arrangement around the metal centre. However, why did a ^{1}H NMR spectrum of complex **1** at room temperature reveal no resonances for the *ortho* phenyl protons of the pendant arm? This should be manifested as fluxional behaviour in variable-temperature NMR spectra. The variable-temperature ^{1}H NMR of **1** from +20 to −50 °C as shown in Fig. 2 confirmed the fluxionality of the ligand. Although ^{1}H NMR spectrum of the 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzothiazoline starting material reveals one resonance at δ 7.40 due to equivalent *ortho* phenyl protons, interestingly the spectrum of **1** at −50 °C contains two sharp singlets at δ 7.04 and 9.86 due to inequivalent *ortho* phenyl protons. Especially, one *ortho* proton appears to be shifted downfield, showing the interaction between it and the metal centre.[4] This inequivalence of the protons in the *ortho* position of the 3,5-di-*tert*-butyl-4-hydroxyphenyl group of complex **1** indicates that the pendant arm is held fixed in space or moves very slowly relative to the NMR timescale. Furthermore, the X-ray study of **1** shows that the *tert*-butyl

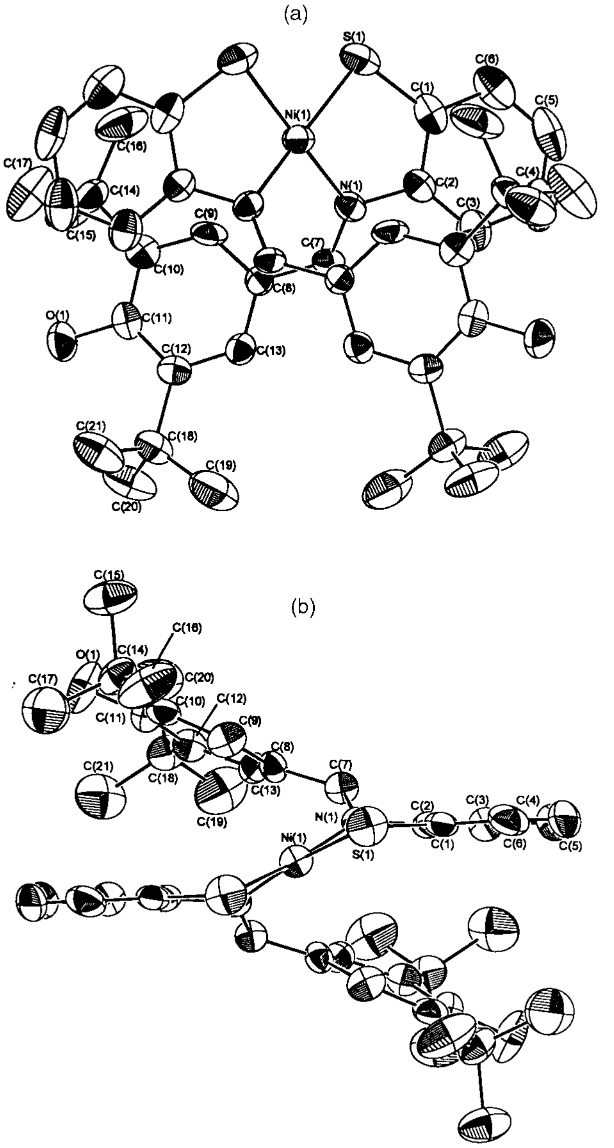


Fig. 1 (*a*) An ORTEP[9] drawing of complex **1** with 50% probability ellipsoids. (*b*) Side view. H atoms are omitted for clarity.

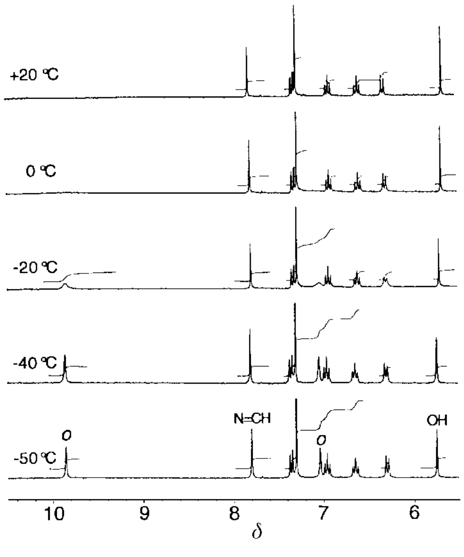


Fig. 2 Variable-temperature ^{1}H NMR spectra of complex **1** in $CDCl_3$ from +20 to −50 °C (*o* = *ortho* protons of pendant arm).

Table 3 Interatomic contacts (Å) in complexes **1** and **2**

1			
C17 ··· C1[a]	4.40(4)	C17 ··· C5[a]	3.87(4)
C17 ··· C2[a]	4.26(4)	C17 ··· C6[a]	4.25(4)
C17 ··· C3[a]	3.87(4)	C17 ··· ring centre[a]	3.81
C17 ··· C4[a]	3.64(4)		
2			
C28 ··· C1	3.875(12)	C27 ··· C21	3.891(13)
C28 ··· C2	3.928(12)	C27 ··· C22	3.948(13)
C28 ··· C3	3.936(12)	C27 ··· C23	3.943(13)
C28 ··· C4	3.919(13)	C27 ··· C24	3.911(14)
C28 ··· C5	3.910(13)	C27 ··· C25	3.886(14)
C28 ··· C6	3.866(13)	C27 ··· C26	3.872(14)
C28 ··· ring centre	3.65	C27 ··· ring centre	3.66

[a] Interatomic contact related to the twofold axis.

substituent of the pendant arm is close to the 2-aminobenzenethiol moiety; the distance between C17 and the centre of the benzene ring C1*–C6* is 3.81 Å (Table 3). It seems reasonable to assume that the *tert*-butyl group in the *meta* position of the pendant arm prevents the observation of the resonances for the *ortho* phenyl protons at room temperature through an attractive interligand interaction between it and the 2-aminobenzenethiol moiety. Such an attractive interaction between CH (soft acids) and π groups (soft bases) is called a CH/π interaction.[10] It has reported that the CH/π interaction plays an important role in determining the conformation of organic compounds,[11] in host–guest complexation[12] and in protein structures.[13] Okawa also suggested the presence of a CH/π interaction in co-ordination compounds.[14] Thus, dynamic behaviour in the ^{1}H NMR spectra of complex **1** can be correlated to the interligand CH/π interaction. Furthermore, these facts allow us to suggest that the difference in reactivity for carbon–carbon bond formation owing to the substituent group of the pendant arm is also caused by this CH/π interaction.

To probe the presence of the CH/π interaction between ligands in nickel(II) complexes with *meta*-substituted phenyl groups like **1**, complex **2** with a methyl group and **3** with a chlorine atom at the *meta* position have been prepared. Complex **2** was characterized by NMR spectroscopy as well as by crystal structure determination. The molecular structure is shown in Fig. 3. The geometry around nickel is distorted square planar and the two ligands are co-ordinated in a *cis* fashion. Three possible structures accompanying the restriction of rotation of the pendant phenyl group can be anticipated for the *cis* isomer as shown in Scheme 3. Complex **2** has the structure (**I**) in Scheme 3 and the methyl group of pendant arm lies over the aromatic ring of another ligand with separations of 3.65 and 3.66 Å, which are comparable to those reported for complexes showing CH/π interactions (Table 3).[14] The ^{1}H NMR resonance of the methyl group of complex **2** shows an upfield shift when compared with that of the 2-(*m*-toluyl)benzothiazoline starting material. This is explained in terms of an additional ring-current effect caused by an approach of the methyl group to the aromatic ring of the 2-aminobenzenethiol moiety. In addition, the neighbouring *ortho* proton for the methyl group shows a downfield shift (δ 9.60) which is illustrative of the interaction between the proton and the metal centre[4] and a doublet for another *ortho* phenyl proton appears at δ 7.59, which corresponds to a normal phenyl proton (Fig. 4). These results suggest that the structure (**I**) is also predominant in solution.

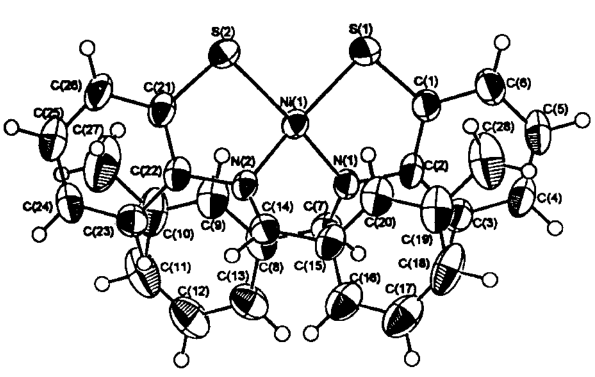


Fig. 3 An ORTEP drawing of complex **2** with 50% probability ellipsoids.

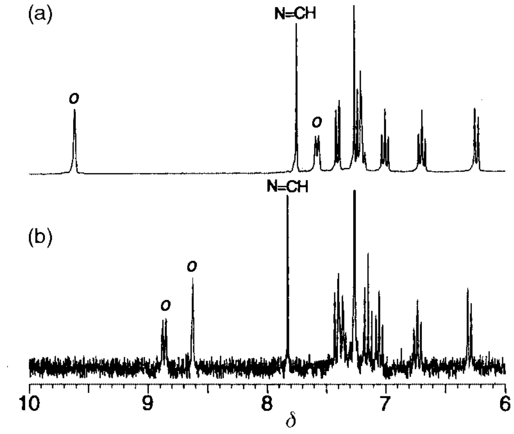
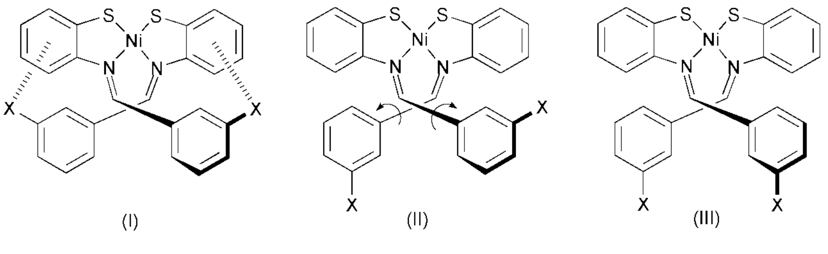


Fig. 4 ^{1}H NMR spectra of complexes **2** (*a*) and **3** (*b*) in $CDCl_3$ (*o* = *ortho* protons of pendant arm).

We could not grow X-ray-quality crystals of complex **3**, but its identity was confirmed by microanalysis and NMR spectroscopy. In the ^{1}H NMR spectrum the azomethine protons are observed as a sharp singlet at δ 7.82. Its spectroscopic properties are in accord with C_2 symmetry. A singlet at δ 8.62 and a doublet at δ 8.86 assigned to the *ortho* protons of the 3-chlorophenyl pendant arm are shifted downfield relative to the phenyl group, which indicates the interaction between these protons and the metal centre (Fig. 4).[4] This behaviour is unexpected for a *trans* isomer[5] and shows the formation of the *cis* isomer for **3**. In addition, such similar chemical shifts (δ 8.62 and 8.86) of two *ortho* phenyl protons indicate that these protons are in similar environments in contrast to the *ortho* protons of complex **2**. Consequently, it can be assumed that



X = Me (**2**), Cl (**3**)

Scheme 3

complex **3** with no CH/π interaction is in equilibrium (structure (**II**)) between structures (**I**) and (**III**) in solution. Thus the results presented here for complexes **2** and **3** reveal that such an anomalous arrangement of **2** with respect to the methyl group (structure (**I**)) is enforced by the CH/π interaction.

In conclusion, through an examination of complexes **2** and **3**, the reactivity towards carbon–carbon bond formation and dynamic behaviour in the ^{1}H NMR spectra of **1** is interpreted in terms of an interligand CH/π interaction.[15]

References

1 L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 1967, **1**, 365; L. F. Lindoy, D. H. Busch and V. Goedken, *J. Chem. Soc.*, *Chem. Commun.*, 1972, 683.

2 T. Kawamoto and Y. Kushi, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 3137.

3 T. Kawamoto, H. Kuma and Y. Kushi, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1599.

4 T. Kawamoto, I. Nagasawa, H. Kuma and Y. Kushi, *Inorg. Chem.*, 1996, **35**, 2427.

5 I. Nagasawa, T. Kawamoto, H. Kuma and Y. Kushi, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1337.

6 P. J. Palmer, R. B. Trigg and J. V. Warrington, *J. Med. Chem.*, 1971, **14**, 248.

7 CRYSTAN-GM, A Computer Program for the Solution and Refinement of Crystal Structures for X-ray Diffraction Data, MAC Science Corporation, Yokohama, 1994.

8 SIR 92, A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

9 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

10 M. Nishio and M. Hirota, *Tetrahedron*, 1989, **45**, 7201; M. Nishio, M. Hirota and Y. Umezawa, *The CH/π Interaction. Evidence, Nature and Consequences*, John Wiley & Sons, Inc., New York, 1998.

11 J. A. Dickinson, P. W. Joireman, R. T. Kroemer, E. G. Robertson and J. P. Simons, *J. Chem. Soc.*, *Faraday Trans.*, 1997, 1467.

12 T. Fujimoto, R. Yanagihara, K. Kobayashi and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2113.

13 M. Nishio, Y. Umezawa, M. Hirota and Y. Takeuchi, *Tetrahedron*, 1995, **51**, 8665.

14 H. Okawa, *Coord. Chem. Rev.*, 1988, **92**, 1; K. Yamanari, T. Nozaki, A. Fuyuhiro, Y. Kushi and S. Kaizaki, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2851; K. Jitsukawa, K. Iwai, H. Masuda, H. Ogoshi and H. Einaga, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3691.

15 Complexes **2** and **3** lead to the corresponding nickel complexes with non-innocent ligands in contrast to **1**. This result can be attributed to a multiple CH/π interaction by the *tert*-butyl group of **1** (CH/π interaction; *tert*-butyl group > methyl group).