Three Types of Nickel(II) Complexes Derived from 2-Substituted Benzothiazoline; Formation of a Tetranuclear Complex by a Sterically Induced Orthometallation Reaction

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The reaction of 2-(2,4-dichlorophenyl)benzothiazoline with nickel(II) acetate tetrahydrate in ethanol has afforded the monohelical bis[2-(2,4-dichlorophenylmethyleneamino)benzenethiolato]nickel(II) ([Ni(HL^1)$_2$] (**1**)). The X-ray structure of **1** has revealed that *ortho*-phenyl hydrogen atoms of pendant arms are oriented to the nickel center in a monohelical structure. The low-field resonance for their *ortho*-protons in the ^{1}H NMR spectrum indicates that the Ni···H–C interaction is maintained in solution. Heating **1** in toluene gave a square-planar nickel(II) complex with a non-innocent ligand ([Ni(L^2)] (**2**)), and prolonged heating yielded a thiolato-bridged tetranuclear nickel(II) complex ([Ni$_4$(L^1)$_4$] (**3**)). The tetranuclear complex **3** was formed from activation of the *ortho* C–H bond, not the C–Cl bond, through sterically controlled Ni···H–C contacts in **1**. The molecular structures of **2** and **3** have also been determined by X-ray crystallographic methods.

In general, the reactions of 2-substituted benzothiazolines with metal ions allow the formation of Schiff base complexes with N,S donor atoms.[1–4] The design and synthesis of their complexes remain a subject of intense activity; changes of the substituents on the pendant phenyl rings directly influence the properties and geometry of the metal complexes[2,3] and the observation of cyclometallation, which is undoubtedly one of the extensively researched areas of organometallic chemistry.[4] The cyclometallation of phenyl-substituted ligands, termed orthometallation, in particular, is an important area as a good model for C–H activation. It is well known that palladium(II) complexes readily orthometallate a variety of organic ligands.[5] Several nickel(II) complexes containing orthometallated ligands have also been reported,[5–8] but little is known about orthometallated nickel(II) complexes containing anionic N–C chelates without the cyclopentadienyl ring as a stabilizing ligand, except for potentially tridentate N–C–N ligands.[7] A very small number of nickel(II) complexes with anionic N–C chelates have been prepared by the reactions of nickel(0) complex, [Ni(cod)$_2$], with *ortho* halo-substituted amines or imines.[8] We have reported that a thiolato-bridged tetranuclear palladium(II) complex was formed by orthometallation of the monohelical palladium(II) complex with 1-naphthyl groups as pendant arms through a three-center four-electron M···H–C interaction, like the conventional hydrogen bond,[4] but the formation of a corresponding nickel(II) complex was not observed.

We have mainly reported on three types of metal complexes for Group 10 metals: a mononuclear Schiff base complex,[2,4] a mononuclear complex with a non-innocent ligand,[2b,4b] and a thiolato-bridged tetranuclear complex.[4] However, such three types of complexes have not been simultaneously isolated so far. In this paper, we report on the synthesis and characterization of three types of nickel(II) complexes derived from 2-(2,4-dichlorophenyl)benzothiazoline, including the formation of a tetranuclear nickel(II) complex containing anionic N–C chelate through sterically controlled Ni···H–C contacts in the monohelical nickel(II) complex.

Experimental

General Procedures. All of the synthetic reactions were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. Workup procedures, including column chromatography, were performed in air. The 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 with tetramethylsilane as an internal standard (δ 0) and UV/vis spectra on a JASCO V-570 spectrophotometer. Cyclic voltammograms were performed in a three-electrode cell with a glassy carbon disk as the working electrode, platinum wire as a counter electrode, and a Ag/AgCl reference electrode. They were measured in CH$_2$Cl$_2$ containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate. Elemental analyses were performed at Osaka University.

Synthesis of 2-(2,4-Dichlorophenyl)benzothiazoline. 2-(2,4-Dichlorophenyl)benzothiazoline was prepared according to a literature procedure for 2-substituted benzothiazolines.[9] 2-Aminothiophenol (0.36 g, 2.9 mmol) and 2,4-dichlorobenzaldehyde (0.50 g, 2.9 mmol) in ethanol (20 cm^3) were refluxed for 30 min. The solvent was removed, the residue washed with *n*-hexane and the white solid dried in vacuo. Yield 0.48 g, 60%. Found: C, 55.21; H, 3.29; N, 5.00%. Calcd for C$_{13}$H$_9$Cl$_2$NS: C, 55.33; H, 3.21; N, 4.96%. IR (Nujol) $\nu_{\max}$/cm^{-1} 3334 (NH) and 1582 (aromatic C=C). ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.68 (1H, d, $J = 8.2$ Hz, aryl CH), 7.38 (1H, d, $J = 2.0$ Hz, aryl CH), 7.23 (1H, dd, $J = 8.7$ and 1.8 Hz, aryl CH), 7.04 (1H, d, $J = 7.6$ Hz, aryl CH), 6.97 (1H, td, $J = 7.7$ and 1.2 Hz, aryl CH), 6.82–6.75 (2H, m, aryl CH), 6.59 (1H, d, $J =$

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4.3 Hz, aryl CH), and 4.43 (1H, d, $J = 2.6$ Hz, NH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 145.59, 138.54, 134.14, 131.90, 129.12, 128.15, 127.38, 126.06, 125.37, 121.77, 121.17, 110.55, and 64.92.

Synthesis of Bis[2-(2,4-dichlorophenylmethyleneamino)benzenethiolato]nickel(II) ([Ni(HL^1)$_2$] (1)). To a solution of 2-(2,4-dichlorophenyl)benzothiazoline (1.00 g, 3.54 mmol) in ethanol (50 cm^3) was added nickel(II) acetate tetrahydrate (0.44 g, 1.77 mmol). The reaction mixture was refluxed for 20 min and then cooled to room temperature. The dark reddish-brown precipitate was isolated by filtration and dried in vacuo. Yield 0.94 g, 86%. Single crystals suitable for an X-ray crystal structure analysis were obtained by the diethyl ether diffusion of a chloroform solution. Found: C, 50.53; H, 2.70; N, 4.56%. Calcd for $C_{26}H_{16}Cl_4N_2NiS_2$: C, 50.28; H, 2.60; N, 4.51%. IR (Nujol) ν_{max}/cm^{-1} 1588 (C=N) and 1578 and 1570 (aromatic C=C). ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.79 (2H, d, $J = 8.2$ Hz, aryl CH), 8.12 (2H, s, N=CH), 7.41 (2H, s, aryl CH), 7.40 (2H, dd, $J = 8.6$ and 1.0 Hz, aryl CH), 7.08 (2H, t, $J = 7.4$ Hz, aryl CH), 6.82 (2H, dd, $J = 8.2$ and 2.0 Hz, aryl CH), 6.74 (2H, t, $J = 7.8$ Hz, aryl CH), and 6.39 (2H, d, $J = 7.6$ Hz, aryl CH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 162.69, 149.65, 146.62, 138.58, 134.95, 132.75, 130.86, 129.55, 129.04, 128.85, 127.92, 122.10, and 116.38. UV–vis ($CHCl_3$) $\sigma_{max}/10^3$ cm^{-1} [log($\mathcal{E}$/dm^3 mol^{-1} cm^{-1})]: 19.31sh (3.63), 21.37 (3.69), and 30.03sh (4.24). CV (CH_2Cl_2, 0.1 M [(n-Bu)$_4$N]BF$_4$; E vs Ag/AgCl [V]): $E_{pc} = -0.99$ (irreversible).

Synthesis of [Bis-2,2′-{1,2-bis(2,4-dichlorophenyl)ethylenediimine}benzenethiolato]nickel(II) ([Ni(L^2)] (2)). A suspension of **1** (0.156 g, 0.251 mmol) in toluene (20 cm^3) was refluxed for 30 min and then cooled to room temperature. After filtration, the solvent was removed on a rotary evaporator. The black crystalline product was dissolved in CH_2Cl_2 (20 cm^3) and filtered. The filtrate was purified by chromatography on a silica gel (230–400 mesh) column. The following products were separated, in order of elution, with CH_2Cl_2: the desired complex **2** as a violet band, the starting complex **1** as a reddish-brown band, and a small amount of unidentified material as a brown band that did not move. Yield 0.068 g, 44%. Single crystals suitable for X-ray crystal structure analysis were obtained by n-pentane diffusion of a chloroform solution. Found: C, 50.55; H, 2.81; N, 4.56%. Calcd for $C_{26}H_{16}Cl_4N_2NiS_2$: C, 50.28; H, 2.60; N, 4.51%. IR (Nujol) ν_{max}/cm^{-1} 1585, 1570, and 1557 (aromatic C=C). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.72 (2H, dd, $J = 7.6$ and 1.0 Hz, aryl CH), 7.50 (2H, d, $J = 2.0$ Hz, aryl CH), 7.02–7.23 (8H, m, aryl CH), 6.91 (2H, dd, $J = 8.6$ and 2.3 Hz, aryl CH), and 6.61 (2H, s, CH–CH). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 162.40, 160.16, 138.94, 134.63, 134.10, 131.67, 129.34, 128.71, 128.18, 128.06, 123.27, 119.55, and 76.93. UV–vis ($CHCl_3$) $\sigma_{max}/10^3$ cm^{-1} [log($\mathcal{E}$/dm^3 mol^{-1} cm^{-1})]: 8.73 (3.43), 10.16 (3.39), 11.90 (4.53), 13.59sh (3.89), 16.86 (3.09), 18.42 (3.07), 21.10 (3.09), 28.25 (3.63), and 31.06 (3.75). CV (CH_2Cl_2, 0.1 M [(n-Bu)$_4$N]BF$_4$; E vs Ag/AgCl [V]): $E_{1/2} = -0.09$ (ΔE_p/mV = 96) and $E_{pc} = -1.00$ (irreversible).

Synthesis of Tetrakis[2-N-(2,4-dichlorobenzylidene-κC^2-amino-κN)benzenethiolato]tetranickel(II) ([Ni$_4$(L^1)$_4$] (3)). A suspension of **1** (0.324 g, 0.522 mmol) in toluene (20 cm^3) was refluxed for 1.5 h and then cooled to room temperature. The yellowish-brown precipitate formed (0.214 g) was filtered off.[10] The filtrate was purified by chromatography on a silica gel (230–400 mesh) with CH_2Cl_2 as the eluent. The first dark green band containing **2** and **3** was collected and dried; crystallization from $CHCl_3$–diethyl ether gave **3** with a diamond shape. While this is a reproducible synthetic method of **3**, the crystallized **3** was quite insoluble in common solvents. This property and the yield (<5%) prevented any characterization beyond a crystal structural determination. The formation of **3** by heating of **2** (0.050 g, 0.081 mmol) in toluene (20 cm^3) for 1.5 h was not observed.

X-ray Crystallography. All crystals were mounted on the end of glass fibers with epoxy. X-ray diffraction data for all complexes were collected on a Mac Science MXC3 diffractometer equipped with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at room temperature; θ–2θ scans were employed. Three standard reflections, measured after every 100 scans, showed a non-appreciable loss in intensity during the data collection process. An empirical absorption correction was made on the basis of ψ-scans. The solution and refinement procedures were made by applying the CRYSTAN-GM software package.[11] The structures of **1** and **2** were solved by direct methods using SIR 92[12] and that of **3** was

Table 1. Crystallographic Data for Complexes **1**, **2**, and **3**

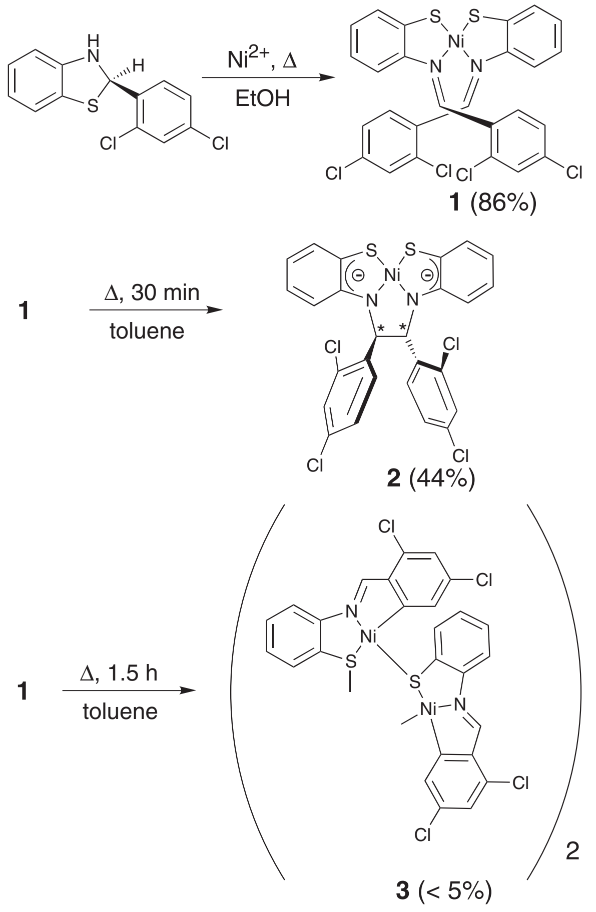
	1	**2**	**3**
Formula	$C_{26}H_{16}Cl_4N_2NiS_2$	$C_{26}H_{16}Cl_4N_2NiS_2$	$C_{52}H_{28}Cl_8N_4Ni_4S_4$
M	621.06	621.06	1355.47
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	10.181(7)	10.188(4)	14.651(7)
b/Å	12.98(1)	15.316(5)	27.14(1)
c/Å	10.179(8)	8.291(5)	13.374(6)
α/°	107.06(6)	93.12(4)	
β/°	97.83(6)	102.58(4)	113.91(3)
γ/°	73.06(6)	85.34(3)	
V/Å^3	1229(2)	1258(1)	4861(4)
Z	2	2	4
μ/mm^{-1}	1.415	1.383	2.188
No. unique reflections measured	2730	5405	3372
No. reflections in refinement	2232 ($I > 2.0\sigma(I)$)	4767 ($I > 2.0\sigma(I)$)	1822 ($I > 2.0\sigma(I)$)
R	0.070	0.078	0.087
R_w	0.087	0.100	0.107

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, weighting scheme: $1/[\sigma^2(F_o) + 0.01F_o{}^2]$ for **1** and **3** and $1/[\sigma^2(F_o) + 0.001F_o{}^2]$ for **2**.

solved by PATTY in DIRDIF 92,[13] followed by successive cycles of least-squares refinement and difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were calculated with a C–H distance of 0.96 Å. The hydrogen atoms of **1** and **2** were refined isotropically, but those of **3** were not refined. Crystallographic data are listed 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 153392–153394.

Results and Discussion

The reaction of $Ni(CH_3COO)_2 \cdot 4H_2O$ with 2-(2,4-dichlorophenyl)benzothiazoline in ethanol yielded a dark reddish-brown precipitate of nickel(II) complex ($[Ni(HL^1)_2]$ (**1**)). Heating of **1** in toluene for 30 min gave a square-planar nickel(II) complex with a non-innocent ligand ($[Ni(L^2)]$ (**2**)) through carbon–carbon bond formation, and prolonged heating afforded the thiolato-bridged tetranuclear nickel(II) complex ($[Ni_4(L^1)_4]$ (**3**)) (Scheme 1). Complex **3** was contaminated with **2** even after column chromatography, and obtained in a low yield only by crystallization from $CHCl_3$–diethyl ether. It is presumed that **3** is directly derived from **1** because the formation of **3** by heating of **2** was not observed. Muller et al. have reported the synthesis of [NiX(C–N–N′)], $[Ni(C–N–N′)L]^+$, and [NiX(C–N)L] containing anionic N–C chelates by the reactions of $[Ni(cod)_2]$ with *ortho* halo-substituted amines or imines.[8] These complexes were prepared by the oxidative addition of Ni(0) to the *ortho* C–X bonds (X = Cl or Br), not activation of the *ortho* C–H bond. In contrast, **3** was obtained by the activation of C–H bonds, not C–Cl bonds. This behavior can be related to a difference in the reactivity between the Ni(0) and Ni(II) species for the C–X and C–H bonds. In addition, the nickel(II) complex derived from 2-phenylbenzothiazoline with the unsubstituted phenyl group did not give the corresponding thiolato-bridged tetranuclear nickel(II) complex under identical experimental conditions. This suggests that chlorine-substituted phenyl pendant arms are necessary to yield the orthometallated product.



Scheme 1.

A general view of **1** which defines the atom numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. Complex **1** comprises of a slightly distorted square-planar nickel(II) site with *cis* nitrogen and *cis* sulfur atoms (dihedral angle between S–Ni–N planes is 25(3)°), and shows a monohelical geometry accompanying the crossing of pendant arms. The Ni–S and Ni–N bond distances are normal.[2,3] Once the rotation of pendant arms in the complex **1** is restricted, there is a possibility of three isomers as shown in Scheme 2. Complex **1** forms an isomer (I), where *ortho*-phenyl

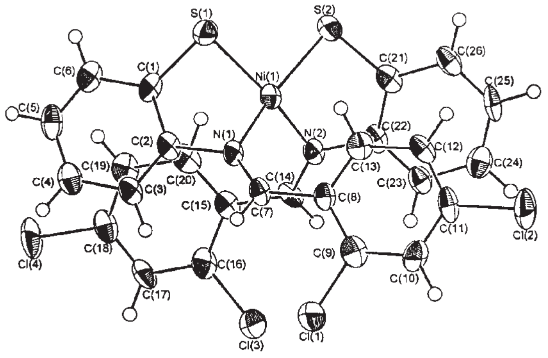
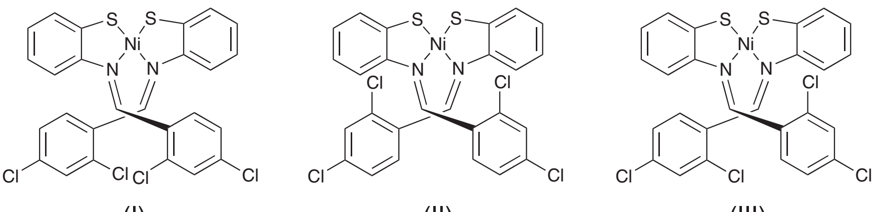


Fig. 1. Molecular structure of complex **1**.

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

	1	**2**
Ni1–S1	2.184(5)	2.130(2)
Ni1–S2	2.181(5)	2.128(2)
Ni1–N1	1.928(12)	1.805(5)
Ni1–N2	1.939(12)	1.824(4)
S1–C1	1.761(16)	1.735(6)
S2–C21	1.765(16)	1.706(5)
N1–C2	1.454(18)	1.356(6)
N1–C7	1.282(18)	1.453(7)
N2–C14	1.299(18)	1.448(6)
N2–C22	1.434(18)	1.361(6)
S1–Ni1–S2	94.7(2)	94.6(1)
S1–Ni1–N1	86.3(4)	89.4(2)
S1–Ni1–N2	162.8(4)	175.5(2)
S2–Ni1–N1	162.7(4)	176.0(2)
S2–Ni1–N2	86.0(4)	89.7(2)
N1–Ni1–N2	98.2(5)	86.2(2)
Dihedral angle between NiNS planes	25(3)	1(3)



(I) (II) (III)

Scheme 2.

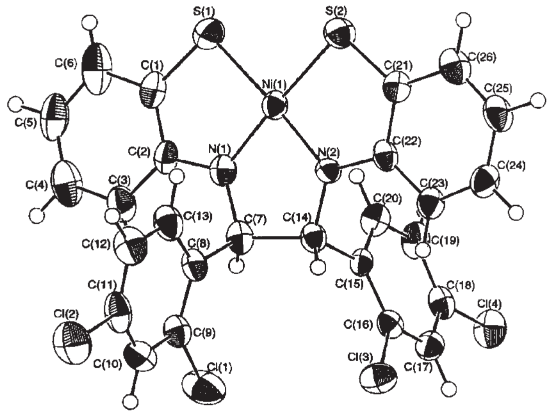


Fig. 2. Molecular structure of complex **2**.

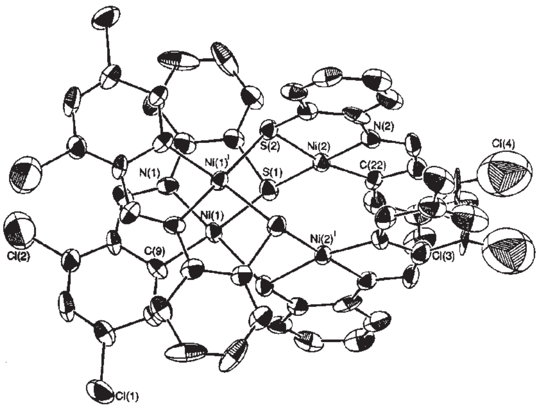


Fig. 3. Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex **3**

Ni1–S1	2.215(16)	S1–Ni1–S2′	95.0(6)
Ni1–S2′	2.207(16)	S1–Ni1–N1	87.5(15)
Ni1–N1	1.91(5)	S1–Ni1–C9	166.6(17)
Ni1–C9	1.93(6)	S2′–Ni1–N1	176.1(14)
Ni2–S1	2.179(17)	S2′–Ni1–C9	94.1(17)
Ni2–S2	2.235(16)	N1–Ni1–C9	84.0(22)
Ni2–N2	1.91(5)	S1–Ni2–S2	95.7(6)
Ni2–C22	1.92(6)	S1–Ni2–N2	176.2(15)
S1–C1	1.77(6)	S1–Ni2–C22	93.0(16)
S2–C14	1.75(6)	S2–Ni2–N2	87.8(15)
N1–C2	1.42(8)	S2–Ni2–C22	169.1(16)
N2–C15	1.45(8)	N2–Ni2–C22	83.4(21)
Ni1···Ni1′	3.101(9)		
Ni1···Ni2	3.629(10)		
Ni1···Ni2′	3.745(10)		
Ni2···Ni2′	3.093(9)		

Symmetry operator for primed atoms: $-x$, y, $-1/2-z$.

hydrogen atoms are oriented to the nickel center. In addition, the Ni(1)···H–C(13) and Ni(1)···H–C(20) in **1** have short contacts of 2.46(2) Å and 2.48(2) Å, showing some interactions between these atoms.[3,4,14] The low-field shift of the *ortho*-phenyl protons in the ^{1}H NMR spectrum of **1** confirms this interaction (vide infra).

A molecular view of **2** with the atomic numbering scheme is displayed in Fig. 2. The nickel atom is in a square-planar environment with a dihedral angle between the S–Ni–N planes of 1(3)°. The Ni–S bond distances (2.130(2) and 2.128(2) Å) and the Ni–N bond distances (1.805(5) and 1.824(4) Å) are shorter than those observed in Ni–thiolato and Ni–imine complexes, such as **1**, but are comparable to those reported for nickel(II) complexes with non-innocent ligands (Table 2).[2b] Indeed, the S–C bond distances of 1.735(6) and 1.706(5) Å and the N–C bond distances of 1.356(6) and 1.361(6) Å are strongly indicative of the charge distribution nature of the non-innocent nickel(II) complexes.[2b,15b] Thus, the structure determination unambiguously shows that the 2-aminothiophenol moieties result in a non-innocent ligand. The UV–vis absorption spectrum and cyclic voltammogram of **2** support this result (vide infra). Wieghardt et al. have shown that the electronic structures of analogous species containing a diamagnetic d^8 central ion are best described as singlet diradicals based on structural and spectroscopic criteria.[15] It is thought that the spins in **2** are also intramolecularly antiferromagnetically coupled, as shown in the ^{1}H NMR spectrum without any detectable paramagnetic shifts or line broadening (vide infra).[16]

The brown crystals of **3** were of poor quality; nevertheless, it was possible to confirm the structural arrangement by X-ray crystallography. A perspective drawing with the adopted numbering scheme is shown in Fig. 3 and selected bond parameters are given in Table 3. This molecular structure has a crystallographically imposed twofold axis. This structure is very similar to that of the palladium(II) complex previously studied; also, the core consists of a Ni_4S_4 eight-membered ring bridged by sulfur atoms.[4] To our knowledge, **3** is the first nickel(II) complex with orthometallated the C,N,S-tridentate ligand that has been confirmed by X-ray crystallography. Each nickel atom is in a slightly distorted square-planar coordination environment. The Ni–C bond distances of 1.93(6) and 1.92(6) Å and the Ni–N bond distances of 1.91(5) Å in the five-membered orthometallacycle compare with those found in other Ni(II) complexes with anionic N–C chelates.[8] The Ni–S distances of 2.179(17)–2.235(16) Å are relatively longer than those of **1** and other related complexes.[2,3] Furthermore, the *trans* influence of the metalated carbon can be reflected in the lengthening of the Ni–S distances *trans* to the carbon atom (2.215(16) and 2.235(16) Å) with respect to the Ni–S distances *trans* to the imine nitrogen (2.207(16) and 2.179(17) Å). A long Ni···Ni separation (3.09–3.75 Å) suggests that there is no Ni–Ni interaction.

In the ^{1}H NMR spectrum of complex **1**, the azomethine protons appear as one singlet at 8.12 ppm. In addition, the 2-iminothiophenolato protons appear as two doublets and two triplets and the pendant arms exhibit two doublets and one singlet. These results indicate the C_2 symmetrical structure of **1** in $CDCl_3$. The most striking feature is the extremely low-field shift (10.79 ppm) of the pendant *ortho*-phenyl protons. This low-field resonance can be attributed to the three-center four-electron Ni···H–C interaction, which suggests that the isomer (I) in Scheme 2 for **1** is also predominant in solution. The ^{1}H NMR spectrum of **2** gives one sharp singlet due to the protons of the asymmetric carbon atoms, which were generated by carbon–carbon bond formation, at 6.61 ppm. The UV–vis absorption spectrum of **1** is dominated by two large charge transfer transitions at ca. 20×10^3 cm^{-1}, which obscure the d–d transition. In contrast to **1**, the spectrum of **2** reveals a very strong absorption band at ca. 12×10^3 cm^{-1}, which is the characteristic absorption for metal complexes with non-innocent ligands.[2b,15] The cyclic voltammograms of **1** and **2** display irreversible reduction waves at -0.99 and -1.00 V, respectively, which are expected to be a metal-centered reduction ($Ni^{II} \rightarrow Ni^{I}$).[2b] The most significant feature in the cyclic voltammetric studies is that **2** exhibits one reversible redox wave at $E_{1/2} = -0.09$ V. This process is a ligand-centered one-electron redox change, which is a characteristic feature for non-innocent ligands.[2b,15] The corresponding redox wave was not observed for **1** without a non-innocent ligand. Thus, these features of **1** and **2** were consistent with the proposed structures, which were confirmed by the X-ray analysis of single crystals. Complexes **1** and **2**, which have the same chemical compositions, can be correlated in a valence isomerism.

In conclusion, by using 2-(2,4-dichlorophenyl)benzothiazoline as a starting material, three types of nickel(II) complexes were completed. The monohelical nickel(II) complex **1** is first isolated by the reaction of nickel(II) acetate tetrahydrate with 2-(2,4-dichlorophenyl)benzothiazoline. X-ray and ^{1}H NMR studies of **1** indicate that the *ortho*-phenyl hydrogen atoms lie over the nickel center, and that the Ni···H–C interaction is maintained even in solution. The heating of **1** gives a square-planar nickel(II) complex with a non-innocent ligand **2**. Furthermore, a prolonged heating of **1** leads to orthometallation by activation of the *ortho* C–H bond, not the C–Cl bond, of the pendant arm to give the thiolato-bridged tetranuclear nickel(II) complex **3**. This behavior is in contrast to the formation of five-membered nickelocycles through the oxidation addition of the *ortho* C–X bonds (X = Cl or Br) by the reaction of Ni(0) species with *ortho* halo-substituted ligands. It can be assumed from these results that the sterically induced Ni···H–C contacts allow the formation of **3** by activation of the *ortho* C–H bond.

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