Inorg. Chem. **1999,** *38,* 4329−4333

A New Method for Incorporating Thiolate Donors into a Metal Coordination Sphere. Synthesis and Crystal Structures of the First Nickel Complexes of an N_3S Ligand

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Received May 6, 1999

A new method for the synthesis of metal complexes with thiolate coordination is described which eliminates the need for protection/deprotection of the thiol. The reaction in methanol of 2,2′-dithiodibenzaldehyde with nickel(II) complexes containing coordinated primary amines results in the concomitant Schiff-base condensation and cleavage of the disulfide bond to form a chelating amine/thiolate ligand. This method is used to synthesize nickel(II) complexes with varying N/S donor sets, including the first structurally characterized nickel complexes of tetradentate N_3S ligands. $[Ni(C_{11}H_{16}N_3S)]BPh_4$ crystallizes in monoclinic $P2_1$ ($a = 9.128(2)$ Å, $b = 15.219(5)$ Å, $c = 10.317(4)$ Å, $\beta = 110.23(2)°$, $Z = 2$); $[Ni(C_{14}H_{22}N_3S)]BPh_4$ crystallizes in orthorhombic $P2_12_12_1$ ($a = 9.894(2)$ Å, $b = 16.687(4)$ Å, $c = 21.807(7)$ Å, $Z = 4$).

Introduction

A considerable amount of attention is currently being shown in the synthesis of geometrically distorted Ni(II) complexes with mixed N and S donor sets.[1] Nickel is present in the active sites of several important classes of metalloproteins, as either a homodinuclear or a heterodinuclear species. The active site of 2-mercaptoethanol-inhibited urease[2] contains two Ni centers bridged by thiolate donors, while thiolate bridging between Ni and Fe centers is present in the Ni/Fe hydrogenases.[3] The nickel coordination sphere in both of these metalloenzyme systems contains N and S donor atoms in unusual 5- or 6-coordinate arrangements with significant distortions from regular geometry. These distorted configurations often give rise to Ni centers with reversible Ni^{II}/Ni^{I} and Ni^{III}/Ni^{II} couples and low Ni^{III}/Ni^{II} redox potentials, characteristics which are crucial to the activity of the enzymes. These unusual structural and electronic features have led to increased interest in the synthesis of Ni(II) complexes with mixed N/S donating chelates as structural and spectroscopic models of the active sites.

Metal complexes with mixed N/S donating atoms are normally synthesized in two steps: (1) synthesis of N/S containing ligands and (2) metal complexation. This method usually necessitates protection and deprotection of thiols in order to avoid oxidation. Very few examples are found in the literature in which a disulfide group is used for the introduction of thiolate donors without affecting the oxidation state of the metal ions. Livingstone et al. reported the synthesis of a ligand containing a Schiff base and a disulfide moiety which, when reacted with various nickel(II) salts, resulted either in formation of a complex with a coordinated disulfide or in cleavage of the disulfide.[4] In this paper we report a novel Schiff-base semitemplate synthetic strategy for Ni(II) complexes with mixed N/S donating chelates in which a disulfide compound is used as a source of thiolates. This method involves the reaction in methanol of Ni(II) complexes containing coordinated primary amine chelates with 2,2′-dithiodibenzaldehyde, which has both a disulfide group and aldehyde functionalities. By a mechanism involving concomitant Schiff-base condensation and solvent-assisted S−S bond cleavage, new Ni(II) thiolate complexes are formed. We report herein the use of this method for the synthesis of Ni(II) complexes containing three different donor sets: NS_3, N_2S_2, and N_3S, including the first structurally characterized nickel complexes of an N_3S ligand.

Experimental Section

Reagents and Materials. All reagents and solvents were purchased from Aldrich Chemical Co. and Fisher Scientific. All reagents were used without further purification. All solvents were dried (using CaH_2 for CH_2Cl_2, Na for THF, and $Mg(OMe)_2$ for MeOH) and deoxygenated before use. 2,2′-Dithiodibenzaldehyde (DTDB),[5] [Ni(aminothiophenolate)$_2$] (**IC1**),[6] [Ni(2-aminoethanethiolate)$_2$] (**IC2**),[7] [Ni(ethylenediamine)$_3$]Cl$_2$ (**IC3**),[8] and [Ni(diethylenetriamine)$_2$]Cl$_2$ (**IC4**)[9] were synthesized by literature methods.

Physical Measurements. UV−vis spectra were recorded on a Shimadzu UV−vis spectrophotometer (UV-1601). FT-IR spectra were obtained as KBr pellets on a Perkin-Elmer model 1600 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Varian Inova spectrophotometer. Cyclic voltammograms were recorded on an

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10.1021/ic990492k CCC: $18.00

Table 1. Crystallographic Data

	4	**5**
formula	$NiC_{35}H_{36}BN_3S$	$NiC_{38}H_{42}BN_3S$
fw (g/mol)	599.50	641.51
cryst dimens (mm)	0.40 × 0.40 × 0.30	0.40 × 0.40 × 0.40
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
cryst color	red	dark green
a, Å	9.128(2)	9.894(2)
b, Å	15.219(5)	16.687(4)
c, Å	10.317(4)	21.807(7)
β, deg	110.23(2)	
V, Å^3	1474.6(7)	3264(1)
Z	2	4
ρ_{calc}, g/cm^3	1.352	1.299
T, °C	−110	−110
μ(Mo Kα), cm^{-1}	7.59	6.86
λ, Å	0.710 69	0.710 69
R^a ($I > 2\sigma(I)$)	0.048	0.030
R_w^b ($I > 2\sigma(I)$)	0.054	0.036
GOF	2.87	1.57

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

EG & G PAR potentiostat/galvanostat model 263A using a platinum disk working electrode, a platinum gauze counter electrode, and a standard Ag/AgCl reference electrode. Ferrocene was used as an internal standard. Elemental analyses were performed by M-A-H Laboratories, Phoenix, AZ.

X-ray Crystallography. All of the crystal structures reported in this paper were performed on an Enraf-Nonius CAD4 diffractometer controlled by software running on an SGI O2 computer. The crystals were affixed to the tip of a glass fiber with Paratone-N oil (Exxon) and then transferred to the cold stream of the diffractometer operating at −110 °C. The unit cells were determined from the setting angles of 24 reflections with $20° < 2\theta < 24°$ and confirmed by axial photographs. For **4**, 2145 reflections were collected ($\omega-2\theta$; $+h,+k,\pm l$; $2° \leq 2\theta \leq 45°$), giving a unique set of 2008 reflections ($R_{int} = 0.100$) and 1886 observed reflections ($I > 2\sigma(I)$). For **5**, 3214 reflections were collected ($\omega-\theta$; $+h,+k,+l$; $2° \leq 2\theta \leq 45°$), giving a unique set of 2485 reflections ($R_{int} = 0.031$) and 2237 observed reflections ($I > 2\sigma(I)$). The data were processed and the structures solved and refined using the TeXsan package.[10] The data were corrected for secondary extinction (1.49868×10^{-6} for **4** and 1.43544×10^{-7} for **5**), Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans of three intense reflections. The structures were solved by direct methods,[11] and refined by full-matrix least-squares techniques with values for Δf and $\Delta f'$ from Creagh and McAuley.[12] All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were included at idealized positions, but were not refined. Pertinent details are given in Table 1.

Bis[(3,3′-diamino-*N*-methyldipropylamino)dichloronickel(II)] (IC5). To a solution of 500 mg (3.44 mmol) of 3,3′-diamino-*N*-methyldipropylamine in 100 mL of MeOH in a 250 mL round-bottom flask was added $NiCl_2 \cdot 6H_2O$ (409 mg, 1.72 mmol), and the mixture was stirred for 2 h at room temperature. Diethyl ether was added to obtain the green solid product, which was recrystallized from MeOH, washed several times with diethyl ether and cold MeOH, and dried under vacuum (1.054 g, 56%). Anal. Found (calcd for $C_{14}H_{38}Cl_4N_6Ni_2$): C, 30.70 (30.59); H, 6.73 (6.97); N, 15.32 (15.29). The compound has been identified by X-ray crystallography as a dichloro-bridged dimer.[13]

Bis[(*N*-thiosalicylideneimine-2-thiophenolato)nickel(II)] (1). To a suspension of **IC1** (500 mg, 2.37 mmol) in 200 mL of refluxing MeOH in a 250 mL round-bottom flask was added dropwise under N_2 a solution of DTDB (554 mg, 2.04 mmol) in 5 mL of CH_2Cl_2. After heating at reflux for 2 h the red solution was cooled to room temperature and a red precipitate appeared, which was collected by filtration and washed with MeOH. The precipitate was recrystallized from CH_2Cl_2/Et_2O (50/50) to give 520 mg (1.02 mmol, 86% yield). Single crystals for X-ray diffraction analysis were grown by layering diethyl ether on a solution of the complex in CH_2Cl_2. Anal. Found (calcd for $C_{18}H_{18}N_2Ni_2S_4$): C, 42.23 (43.00); H, 3.85 (3.60); N, 5.32 (5.58). Spectroscopic and crystallographic data were in agreement with literature values.[14] Electrochemistry (CH_3CN, 0.1 M NEt_4ClO_4): $E°_{1/2} = -2.2$ V ($E_a - E_c = 100$ mV), 0.20 V (irreversible).

Bis[(*μ*-*S*-2-thiosalicylideneimineethanethiolato)nickel(II)] (2). To a suspension of **IC2** (600 mg, 1.95 mmol) in 100 mL of refluxing MeOH in a 250 mL round-bottom flask was added under N_2 a solution of DTDB (537 mg, 1.97 mmol) in 5 mL of CH_2Cl_2. After 4 h of reflux during which it turned red, the reaction solution was cooled to room temperature and a red precipitate was deposited, collected by filtration, washed several times with MeOH, and recrystallized from CH_2Cl_2/MeOH (50/50) to give 308.2 g of **2** (0.510 mmol, 52%). X-ray quality crystals were obtained by layering diethyl ether on a solution of the complex in CH_2Cl_2. Anal. Found (calcd for $C_{26}H_{18}N_2Ni_2S_4$): C, 51.65 (51.70); H, 2.80 (3.00); N, 4.47 (4.64). Spectroscopic and crystallographic data were in agreement with literature values.[14]

[*N*,*N*′-Ethylenebis(thiosalicylideneiminato)nickel(II)] (3). To a refluxing solution of **IC3** (1.58 g, 4.79 mmol) was added a solution of DTDB (4.84 g, 17.7 mmol) in 5 mL of CH_2Cl_2. After 1 h of reflux the reaction mixture was allowed to cool to room temperature and a golden precipitate was deposited. The precipitate was isolated by filtration and washed with MeOH and ether. The solid was recrystallized from CH_2Cl_2 to give 1.32 g of **3** (3.70 mmol, 77%). Spectroscopic and crystallographic data were in agreement with literature values.[15]

[(1-Thiosalicylideneimine-4,7-diaminoheptane)nickel(II)] Tetraphenylborate (4). To a refluxing solution of **IC4** (1.2 g, 3.57 mmol) in 100 mL of MeOH in a 250 mL round-bottom flask was added a solution of DTDB (548 mg, 2.01 mmol) in 5 mL of CH_2Cl_2. After 2 h of reflux the red solution was filtered and excess $NaBPh_4$ was added to the filtrate to give a red powder, which was washed with MeOH several times. The cationic product as the BPh_4^- salt was then recrystallized from CH_3CN/MeOH (50/50), washed with diethyl ether a few times, and dried under vacuum to give 1.22 g of **4** (2.03 mmol, 57%). X-ray quality crystals were obtained by layering diethyl ether on the product solution in CH_3CN. Anal. Found (calcd for $C_{35}H_{36}BN_3NiS$): C, 70.01 (70.03); H, 6.14 (6.05); N, 7.10 (7.00). IR (KBr, cm^{-1}): 1611($\nu_{C=N}$), 1573 ($\nu_{C=N}$), 1536 ($\nu_{C-H(aromatic)}$). UV−vis (CH_3CN): λ_{max} (nm) (ϵ, M^{-1} cm^{-1}) 352 (30 000), 422 (7500), 530 (1000). ^{1}H NMR (CD_3CN, δ (ppm)): 2.38−2.95 (m, 8H, C***H*₂**C***H*₂**), 3.74−3.83 (m, 2H, N***H*₂**), 4.1−4.35(s, 1H, N***H***), 6.82−6.87 (m, 4H), 6.98−7.02 (m, 8H), 7.25−7.30 (m, 8H), 7.03−7.11 (m, 2H), 7.43−7.46 (m, 1H) 7.65−7.68 (m, 1H), 7.99 (s, 1H, $SC_6H_4C{=}N$***H***). ^{13}C NMR (CD_3CN, δ (ppm)): 53.00, 56.50, 58.00, 74.00, 124.10, 129.35, 129.40, 133.11, 133.20, 137.00, 139.50, 143.32, 175.00.

[{3-Amino-3′-(2-mercaptosalicylideneimino)dipropylamino}nickel(II)] Tetraphenylborate (5). To a refluxing solution of **IC5** (2.5 g, 4.55 mmol) in 100 mL of MeOH in a 250 mL round-bottom flask under N_2 was added a solution of DTDB (700 mg, 2.57 mmol) in 5 mL of CH_2Cl_2. After refluxing for 2 h the dark green solution was filtered and excess solid tetraphenyl borate was added to the filtrate, yielding a green precipitate. The precipitate was washed with MeOH several times and recrystallized from CH_3CN/MeOH (50/50), washed with diethyl ether, and dried under vacuum to give 1.2 g of **5** (1.87 mmol, 41%). Dark green needle-shaped crystals suitable for X-ray diffraction were obtained by layering of diethyl ether on a solution of the complex in CH_3CN/CH_2Cl_2 (50/50). Anal. Found (calcd for $C_{38}H_{42}BN_3NiS$): C, 71.26 (71.06); H, 6.42 (6.59); N, 6.67 (6.54). IR (KBr, cm^{-1}): 1612 ($\nu_{C=N}$), 1584 ($\nu_{C=N}$), 1533 ($\nu_{C-H(aromatic)}$). UV−vis (CH_3-

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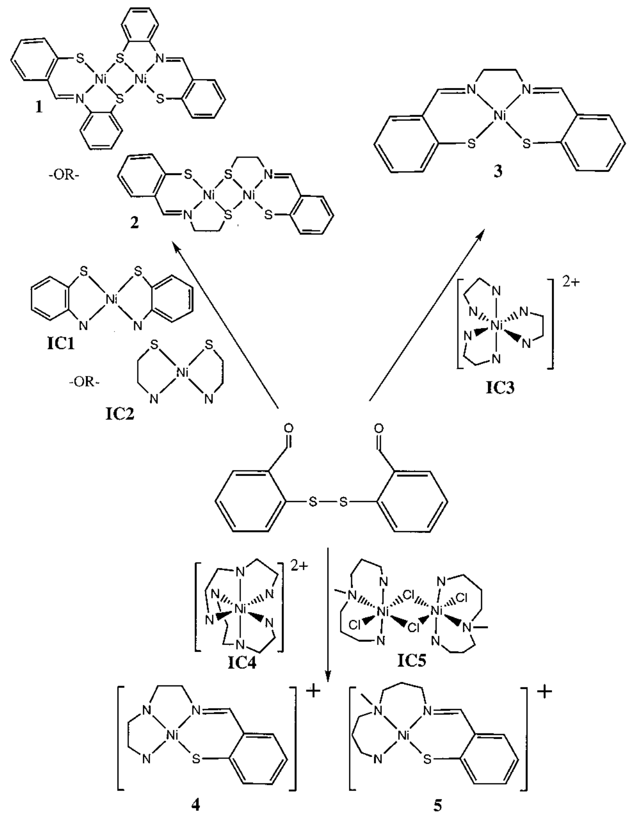
Scheme 1



CN): λ_{max} (nm) (ϵ, M^{-1} cm^{-1}) 245 (16 000), 345 (1200), 420 (1100), 618 (125), 1022 (13).

Results and Discussion

Three different types of Ni(II) complexes have been synthesized by reaction of 2,2′-dithiodibenzaldehyde (DTDB) with three different types of intermediate complexes. The results are summarized in Scheme 1. Reaction with **IC1** and **IC2**, which have only one coordinated amine per ligand, yields the dinuclear complexes **1** and **2**. While this manuscript was in preparation, the syntheses of these complexes by another method and their structures were reported by Bouwman and co-workers.[14] Our crystallographic and spectroscopic analyses of these complexes agree with those previously reported. These complexes result from the Schiff-base condensation of “half” of a 2,2′-dithiodibenzaldehyde with each coordinated primary amine. They adopt a butterfly shape with each nickel atom in an NS_3 coordination environment. The terminal sulfur atoms come from the DTDB reactant, while the bridging sulfur atoms are from the original nickel reactant. Reaction with **IC3**, which provides two coordinated primary amines in each ligand, yields [Ni(tsalen)] (**3**), the synthesis by other methods and structure of which have also been previously reported.[15] In this case, both nitrogen atoms of one ligand have condensed with DTDB, adding a thiosalicylaldehyde group to each side to give **3**, a neutral mononuclear complex with N_2S_2 donation. Finally, reaction with **IC4** and **IC5**, which contain tridentate nitrogen-donor ligands with two coordinated primary amines per ligand, yields the new complexes **4** and **5**. In this case, although two primary amines are available for Schiff-base condensation, reaction of only one amine is realized as this results in a tetradentate ligand that satisfies the preferred four-coordinate geometry of nickel(II) in a N/S environment. The second primary amine thus remains unaltered and the nickel ion is coordinated by an N_3S donor set.

The use of 2,2′-dithiodibenzaldehyde as a reagent in the synthesis of metal complexes containing thiolate coordination has a number of advantages. First is the relative stability of the reactants to air oxidation. DTDB is completely air-stable and is, in fact, an isolated intermediate in the synthesis of thiosalicylaldehyde, while thiosalicylaldehyde must be stored and handled in an inert atmosphere or be protected prior to reaction. An important advantage of this method is the ability to synthesize different types of ligands simply by changing the metal template. In this study, we have demonstrated that three different classes of ligands containing NS_2, N_2S_2, and N_3S donor groups can be synthesized using easily prepared nickel intermediates and the same disulfide reactant. This study was limited to the preparation of tetradentate ligands due to the strong preference of nickel(II) for square-planar coordination in the presence of thiolate ligands. However, the synthesis of **3**, which results from the condensation of DTDB with two coordinated amine groups, demonstrates the utility of this method for incorporating multiple thiolate coordination around a single metal center. Thus, the use of other metals which allow for higher coordination will enable us to use this method for the synthesis of new pentadentate and hexadentate ligands containing thiolate donors.

The reaction between DTDB and the nickel reactants described in this report is observed only in alcoholic solvents.[16] In addition, combination of DTDB and $NiCl_2$ in methanol results in no reaction. Thus, we invoke a mechanism involving both solvent-assisted disulfide cleavage and Schiff-base condensation. Boshi et al. have witnessed a similar mechanism involving the synthesis of Pd−thiolate compounds in which disulfide cleavage is initiated by the nucleophilic attack of methanol on a coordinated disulfide molecule.[17] This reaction occurs with unsubstituted diphenyl disulfide and, lacking a carbonyl group, cannot involve a Schiff-base condensation. There have also been reports in which a preformed Schiff-base ligand containing a disulfide moiety is reacted with a nickel salt in methanol, resulting either in the isolation of a complex with a coordinated, unbroken disulfide[4,18] or in cleavage of the disulfide.[4] The identity of the terminal reductant in this reaction has not been determined, but the fact that the reaction occurs only in alcoholic solvents suggests that the terminal reductant may be methanol. Attack of methanol on a coordinated disulfide molecule initiates the reductive cleavage of the disulfide bond and ultimately results in the release of formaldehyde. Alternatively, the aldehyde functionalite of DTDB could serve as a terminal reductant, being oxidized to the carboxylic acid.

Structure Descriptions. Compounds **4** and **5** are both cationic and have been crystallized as the tetraphenylborate salt. The ORTEP diagrams of the cations are shown in Figure 1 with selected bond distances and angles given in Table 2. They crystallize on general positions in the monoclinic space group $P2_1$ and the orthorhombic space group $P2_12_12_1$, respectively. The nickel is coordinated in approximately square-planar geometry by two amine nitrogen donors and one imine nitrogen donor which derive from the original triamine ligand and one thiolate donor which derives from the DTDB reagent. There are only six literature reports of crystallographically character-

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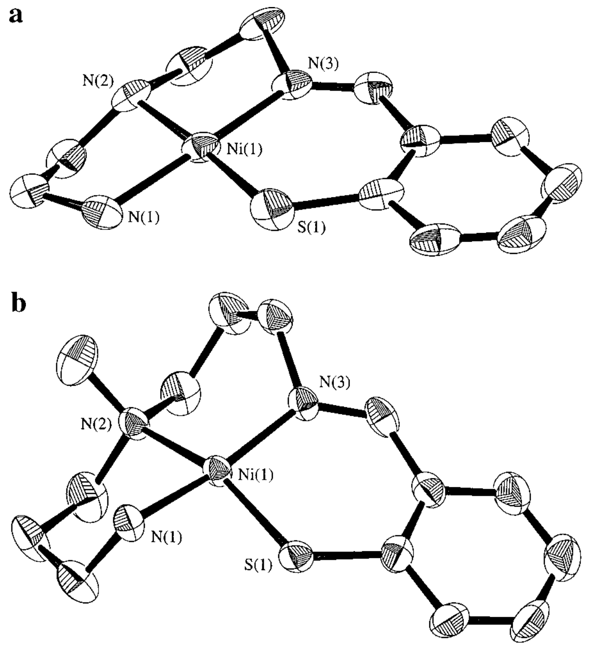

Figure 1. ORTEP drawings of the cations in (a) **4** and (b) **5** showing 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg)

4		**5**	
	Distances (Å)		
Ni(1)−S(1)	2.141(2)	Ni(1)−S(1)	2.144(1)
Ni(1)−N(1)	1.925(7)	Ni(1)−N(1)	1.941(4)
Ni(1)−N(2)	1.909(6)	Ni(1)−N(2)	2.036(3)
Ni(1)−N(3)	1.863(6)	Ni(1)−N(3)	1.877(3)
N(3)−C(5)	1.289(9)	N(3)−C(8)	1.285(6)
N(1)−C(1)	1.49(1)	N(1)−C(1)	1.475(6)
S(1)−C(11)	1.737(8)	S(1)−C(14)	1.742(4)
	Bond Angles (deg)		
S(1)−Ni(1)−N(1)	89.5(2)	S(1)−Ni(1)−N(1)	85.1(1)
S(1)−Ni(1)−N(2)	176.5(2)	S(1)−Ni(1)−N(2)	161.0(1)
S(1)−Ni(1)−N(3)	95.8(2)	S(1)−Ni(1)−N(3)	94.9(1)
N(1)−Ni(1)−N(2)	86.9(3)	N(1)−Ni(1)−N(2)	90.4(1)
N(1)−Ni(1)−N(3)	173.6(3)	N(1)−Ni(1)−N(3)	166.2(2)
N(2)−Ni(1)−N(3)	87.8(3)	N(2)−Ni(1)−N(3)	93.8(1)

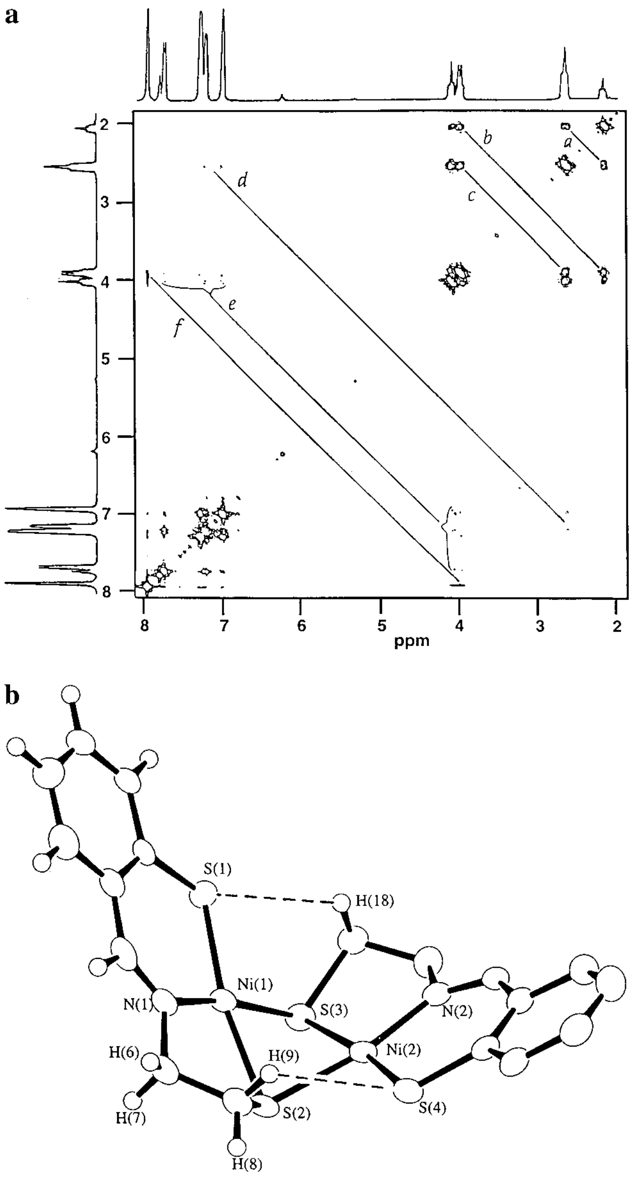

Figure 2. (a) ^{1}H−^{1}H COSY spectrum of **1**. (b) ORTEP diagram of **1** showing the S−H interaction. Non-hydrogen atoms are drawn with 50% thermal ellipsoids. Most of the hydrogen atoms have been omitted.

ized nickel complexes with N_3S coordination,[19,20] and, with the exception of a thiaporphyrin compound,[19c] all of them contain a tridentate N_2S ligand with additional coordination of a nitrogen donor from a second monodentate ligand. Thus, **4** and **5** represent the first crystal structures of four-coordinate nickel complexes with donation from a single non-porphyrinic N_3S ligand. The difference between these two complexes lies in the length of the hydrocarbon backbones; **4** contains two-carbon bridges while **5** contains three-carbon bridges. In addition, the central nitrogen atom in **5** is a tertiary amine, while **4** contains a secondary amine. The resulting structures are very similar, but contain two significant geometric differences. The bond length between Ni and the central nitrogen atom is ≈0.1 Å longer in **5** than in **4**. In fact, the Ni(N_3S) complexes in the literature all have Ni−N bonds ranging in length from 1.833 to 1.934 Å, making the 2.036(3) Å distance between Ni(1) and N(2) in **5** anomalously long. In addition, while **4** displays little deviation from ideal square-planar geometry, **5** is significantly distorted toward tetrahedral geometry, as evidenced by the dihedral angles within the coordination spheres. The angle between the plane defined by Ni(1), N(1), and N(2) and that defined by Ni(1), N(3), and S is only 3.68° in **4**, but increases to 22.0° in **5**. The explanation for this difference lies in the presence of two adjacent six-membered chelate rings in **5**, each of which involves the central nitrogen atom, N(2). In order for both of these rings to assume a chair or boat conformation the coordination environment around the nickel atom must deviate from planarity. In fact, the chelate ring involving the primary amine, N(1), adopts the chair conformation, while the chelate ring involving the imine nitrogen, N(3), adopts a boat conformation. In **4**, the two chelate rings both contain five atoms in which one C atom is ≈0.6 Å out of the plane defined by the other C atom, the two N atoms, and the Ni atom. This allows the

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(20) Bond distances and angles obtained from the Cambridge Structural Database.

coordination environment around the Ni to more closely approach an ideal square-planar geometry.

Electronic Spectroscopy. The observed deviation from regular square-planar geometry is potentially relevant to modeling metalloenzyme active sites. The active sites in hydrogenase enzymes typically display distortions from regular geometry. Such distortions can give rise to important characteristics, such as shifted reduction potentials or altered electronic spectra. A manifestation of this concept is seen in the electronic spectra of **4** and **5**. Compound **4** shows only one d−d ($^1B_{2g} \leftarrow {}^1A_{1g}$) transition at 530 nm, while **5** has two transitions at 618 and 1022 nm. The appearance of the low-energy band can be attributed to the deformation toward a pseudotetrahedral geometry.[21]

NMR Spectroscopy. The ^{1}H−^{1}H COSY spectrum for **1** is shown in Figure 2a, and an ORTEP diagram of **1** with some of the protons labeled is given in Figure 2b.[22] Cross peaks *b* and *c* represent the vicinal couplings between the protons on the ethylene bridge (H(6) and H(7) with H(8) and H(9)) and cross peaks *f* represent the coupling between H(6)/H(7) and the imine proton, identifying the resonances around 4 ppm as being due to H(6) and H(7). Cross peaks *e* represent the expected through-bond coupling of these hydrogens to the phenyl protons. Examination of the features due to H(8) and H(9) displays an interesting interaction that correlates with the solid-state structure of the compound. H(8) and H(9) have significantly different chemical shifts and display strong geminal coupling represented by cross peaks *a*. In addition, H(9) is coupled to some of the phenyl protons (cross peaks *d*), while H(8) shows no such coupling. Both of these features indicate a significantly different environment for H(8) and H(9). These features are explained by inspecting the ORTEP diagram, which shows that the bending of the dimer brings H(9) into relatively close contact with S(4), the sulfur atom of the second ligand. The S···H distance of 2.71 Å is indicative of a weak bonding interaction between sulfur and hydrogen, which allows for the strong geminal coupling between H(8) and H(9), the significant downfield shift of H(9) with respect to H(8), and the observed coupling of H(9) to the phenyl protons. S−H interactions with similar distances have been seen in other nickel(II)−thiolate complexes.[23] These data also indicate that the bent dinuclear geometry observed in the solid-state structure is maintained in solution.

Conclusion. We have demonstrated a novel method using 2,2′-dithiodibenzaldehyde to incorporate chelating thiolate donors into the coordination sphere of a metal ion. This method allows for the synthesis of a number of different types of nitrogen- and sulfur-containing chelating ligands without the need for protection and deprotection of the thiol group. By changing the identity of the metal template, it is possible to synthesize chelating ligands containing nitrogen and sulfur donor atoms in various ratios. Using this method, we have synthesized mononuclear and dinuclear nickel(II) complexes, including the first structurally characterized nickel complexes of a tetradentate ligand with an N_3S donor group. These two complexes show varying amounts of distortion from regular square-planar geometry which is manifest in their electronic spectra. Such distortions may have implications with respect to models for nickel-containing metalloenzymes. This method is not limited to Ni(II) complexes; we are currently investigating analogous reactions with other transition metal ions.

Note Added in Proof. While this manuscript was in press, an alternate synthesis of **4** and the crystal structure of its chloride salt were reported (Bouwman, et al. *Inorg. Chim. Acta* **1999**, *287*, 105).

Acknowledgment. We would like to acknowledge the National Science Foundation (Grant EPS-9550 487) for funding this research. We thank Mr. Hamid Shah for assistance in the preparation of some starting materials.

Supporting Information Available: X-ray crystallographic files containing positional parameters, anisotropic displacement parameters, and all intramolecular distances and angles for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990492K

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[22] The ensuing discussion describes interactions for H(6)−H(9); analogous interactions are present for the symmetry-related protons H(16)−H(19).

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