Synthesis and Characterization of Square Planar Nickel(II)−Arylthiolate Complexes with the Biphenyl-2,2′-dithiolate Ligand

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Two new $Ni^{II}S_4$ complexes with the biphenyl-2,2′-dithiolate ligand (**L**) are reported. The dinuclear complex **1**, $[Ni_2\mathbf{L}_3]^{2-}$, was formed in the reaction of 2−3 equiv of $Na_2\mathbf{L}$ and $[NiCl_4]^{2-}$ and the mononuclear complex $[Ni\mathbf{L}_2]^{2-}$ (**2**) by using 4−10 equiv of $Na_2\mathbf{L}$. Complexes **1** and **2** have been crystallographically characterized. $(Et_4N)_2[\mathbf{1}]\cdot 0.5S_2Ph_2$, CH_3CN: $C_{60}H_{71}N_3Ni_2S_7$, triclinic, $P\bar{1}$, $a = 13.806(2)$ Å, $b = 14.267(2)$ Å, $c = 16.873(2)$ Å, $\alpha = 69.263(10)°$, $\beta = 69.267(8)°$, $\gamma = 83.117(10)°$, $Z = 2$, $R_1 = 0.0752$ (wR2 = 0.2011). $(Et_4N)(Na\cdot CH_3CN)[\mathbf{2}]$: $C_{34}H_{39}N_2NaNiS_4$, triclinic, $P\bar{1}$, $a = 9.9570(10)$ Å, $b = 13.2670(10)$ Å, $c = 13.9560(10)$ Å, $\alpha = 108.489(7)°$, $\beta = 90.396(6)°$, $\gamma = 103.570(4)°$, $Z = 2$, $R_1 = 0.0390$ (wR2 = 0.0995). Both complexes are square planar about the nickel ion in the solid state as well as in solution. Most Ni(II)−thiolate complexes are square planar except the tetrahedral mononuclear complexes with monodentate arylthiolate ligands that cannot force a square planar geometry. The ligand (**L**) has some flexibility to change its bite angle via the phenyl−phenyl bond and should not force a planar geometry on its complexes either. Therefore, it is interesting that **2** has adopted a square planar structure. Complex **2** readily converts to **1** in solution when not in the presence of excess **L** in a process that is presumably similar to that known for other mononuclear, bidentate ligated Ni(II) complexes. Both complexes, at least in the solid state, appear to have an inclination to bind another metal ion on one face of the complex (Ni^{2+} in **1**, Na^+ in **2**). We hope to take advantage of this in future work to synthesize relevant model complexes for the active sites of the nickel−iron hydrogenases after suitable modifications are made to **L**.

Introduction

Nickel was identified as an essential trace element for bacteria over 30 years ago[1] and has since been determined to be required for all forms of life.[2−4] The active sites of the nickel-containing microbial enzymes have very different compositions.[3,5−9] Thus, urease has been found to possess a dinuclear nickel structure with mixed oxygen/nitrogen ligation,[10,11] and methyl−coenzyme M reductase contains a mononuclear tetrahydrocorphinoid-ligated nickel ion (factor F_{430}).[12] Alternatively, carbon monoxide dehydrogenase (CODH) and acetyl-CoA synthase (ACS)[13] plus the recently isolated nickel−superoxide dismutase[3] appear to have both nitrogen (and/or oxygen for CODH/ACS) and sulfur ligation.

Hydrogenases, which catalyze the reversible conversion of dihydrogen to protons and electrons, most frequently contain a nickel center as well as iron−sulfur clusters ([NiFe]-H_2-ase). A few of these also contain a selenium donor to the nickel ion ([NiFeSe]-H_2-ase).[14] In addition, iron-only hydrogenases[15,16] and a hydrogenase that does not contain any metals[17] are known, but these have so far been found to be less widespread.

For many years, the [NiFe]-H_2-ases were believed to possess an active site with a single nickel center that was thought to be bound to cysteine sulfur atoms and probably to nitrogen or oxygen ligands as well.[18] This, of course, caused the small-molecule model chemistry of sulfur and sulfur/nitrogen (or oxygen, etc.) coordinated nickel complexes to be an area of intense interest.[2,19−21] The cysteine−sulfur ligation has been modeled with a variety of thiolate ligands; usually aliphatic thiolate ligands give square planar $Ni^{II}S_4$ complexes and aromatic thiolate ligands that are not constrained to be planar yield tetrahedral $Ni^{II}S_4$ complexes.[2] Here, we report the synthesis and characterization of two unique $Ni^{II}S_4$ complexes with dithiolate ligands that incorporate a biphenyl framework. Interestingly, the complexes maintain a square planar geometry

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about the nickel ion in both the solid and solution states even though they contain aromatic thiolate ligands that do not force a planar geometry upon the ligands.

The rich redox chemistry of the [NiFe]-H_2-ases gave a number of spectroscopically detectable states that were challenging to explain with the single nickel center and were not closely reproduced by mononuclear nickel-containing model complexes.[22] The first hydrogenase crystal structure[23] began to shed light on these issues, since the active site was found to be dinuclear. Compelling evidence that the second metal is iron has since been acquired.[24,25] The [NiFe]-H_2-ase active site contains a nickel center that is bound to four cysteine sulfur ligands, two that are terminally ligated and two that are bridging the nickel and iron centers. The iron ion surprisingly appears to be bound to three diatomic ligands, which were proposed to be two cyanides and a carbonyl ligand[26,27] or an S═O ligand along with two $C{\equiv}O/C{\equiv}N^-$ ligands.[25] In the [NiFe]-H_2-ase structures there is also additional electron density between the two metal sites that could be an oxygen[24] or a sulfur species[25] that may be an artifact of isolation. These crystallized forms probably correspond to one of the states that needs to be transformed into a catalytically competent state, perhaps by loss of the unknown bridging species. The recent structure of a [NiFeSe]-H_2-ase is consistent with this;[28] the structure is similar to those for the [NiFe]-H_2-ases solved thus far except one terminal cysteine ligand is a selenocysteine ligand and there was no bridging oxygen or sulfur species found. The four-coordinate nickel center in the [NiFeSe]-H_2-ase structure is closer in geometry to square planar than tetrahedral (although it is somewhat distorted). The two $Ni^{II}S_4$ complexes reported here do not yet incorporate the iron center seen in the [NiFe]-H_2-ases active site. However, it is interesting that these two complexes seem to exhibit, at least in the solid state, a propensity to attract another metal center to one face of the complex, in one case another Ni(II) ion and in the other a Na^+ ion.

Experimental Section

All manipulations were performed under a dinitrogen atmosphere using standard Schlenk or glovebox techniques at ambient temperature. The solvents were dried (THF and Et_2O with Na/benzophenone; CH_3CN and C_6H_6 with CaH_2; $CHCl_3$ with 4 Å molecular sieves; and DMF with 4 Å molecular sieves and then $MgSO_4$) and freshly distilled under a nitrogen atmosphere from the drying agents before use. $(Et_4N)_2[NiCl_4]$ was prepared as reported,[29] and 2,2′-dimercaptobiphenyl (H_2**L**) was synthesized by modification of a literature procedure.[30] ^1H and ^{13}C NMR spectra were recorded with a Varian Unity Plus 500 MHz FT-NMR spectrometer on freshly prepared solutions at −10 °C. ^1H NMR spectra were referenced to the residual proton resonance of the d_7-DMF solvent (most upfield methyl resonance, δ 2.75) and ^{13}C NMR spectra to the most upfield methyl resonance, δ 29.76. UV−vis spectra were taken with a Hewlett-Packard 8452A diode-array spectrophotometer on freshly prepared solutions, and infrared spectra were acquired on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Elemental analyses were performed by NuMega Resonance Labs, Inc. (San Diego, CA). Cyclic voltammograms were recorded with a BAS-50W potentiostat, and all potentials are quoted relative to the saturated calomel reference electrode. A platinum disk was used as the working electrode, platinum wire as the auxiliary electrode, and $^nBu_4NPF_6$ (0.1 M) as the supporting electrolyte in CH_3CN with a sample concentration of 2.7 mM for **1** and 4.2 mM for **2**. The potential for the ferrocene/ferrocenium couple ($Cp_2Fe/[Cp_2Fe]^+$) as an internal standard was measured to be 0.42 V under the same conditions. Melting points were determined in open glass capillaries with a Thomas-Hoover model 6406-H melting-point apparatus and are uncorrected.

For the X-ray crystallographic studies, suitable crystals were mounted with silicone caulk to a glass fiber on the benchtop. The data were collected with a Siemens P4 diffractometer with a graphite monochromator at ambient temperatures from 3.5 to 45° in 2θ for **1** and from 3.5 to 50° in 2θ for **2**. The structures were solved with direct methods (**2**) or Patterson methods (**1**) followed by subsequent cycles of least-squares refinement and calculation of difference Fourier maps. The data were refined (full-matrix least-squares on F^2) with the Siemens SHELXTL version 5.0.3 PC software package,[31] including its ψ scan based semiempirical absorption correction for both **1** and **2**. Neither structure required an extinction correction. All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed at calculated distances and use a riding model, where the positional and thermal parameters are derived from the carbon atom each hydrogen is bound to while maintaining the calculated distance and optimal angles. For **1** (plate, $\pm h$, $\pm k$, $+l$ collected), 7622 reflections were collected; 6593 independent reflections ($R_{int} = 0.0432$) were used in the refinement for 659 parameters. For **2** (plate, $\pm h$, $+k$, $+l$ collected), 6933 reflections were collected; 5833 independent reflections ($R_{int} = 0.0182$) were used in the refinement for 380 parameters. No peaks or holes of greater than 0.56 $e^-/Å^3$ remained in the final difference maps for the structures. The lattice of structure **1** contains an acetonitrile molecule (the crystal decayed by 33% during data collection presumably because of partial loss of this solvent), as well as half a molecule of the disulfide form of the ligand (which sits on a symmetry element).

Synthesis of $[Et_4N]_2[Ni_2L_3]$ (1). The dithiol H_2**L**[30] (0.463 g, 2.1 mmol) in 15 mL of THF was stirred with sodium metal (>2 equiv) overnight. After filtration to remove the leftover sodium, the solvent was removed in vacuo. The resulting white Na_2**L** was dissolved in CH_3CN (10 mL), and then $[Et_4N]_2[NiCl_4]$[29] (0.466 g, 1.0 mmol) in 30 mL of CH_3CN was added dropwise, giving a dark-brown solution that was left to stir overnight. The volume of the solvent was reduced by two-thirds in vacuo, precipitating brown solids. These solids were filtered and then washed, first with $CHCl_3$ and then with THF (approximately 30 mL each), by stirring each suspension overnight followed by filtration. Three reprecipitations, by dissolution of the solids in a minimum amount of DMF followed by the addition of ≥10 volumes of C_6H_6 dropwise, yielded analytically pure material after filtration and drying under vacuum for a couple of days. Yield: 0.232 g (0.23 mmol, 45%). ^1H NMR: δ 1.30 (t, 24 H, $J = 7$ Hz, $2(CH_3CH_2)_4N$), 3.42 (q, 16 H, $J = 7$ Hz, $2(CH_3CH_2)_4N$), 6.72−6.84 (m, 8 H), 6.89 (~t of d, 2 H, $J = 7$ Hz, 1 Hz), 6.97 (~t of d, 2 H, $J = 7$ Hz, 1 Hz), 7.04 (~t of d, 2 H, $J = 7$ Hz, 1 Hz), 7.31 (m, 4 H), 7.38 (d of d, 2 H, $J = 7$ Hz, 1 Hz), 7.50 (~t of d, 2 H, $J = 7$ Hz, 1 Hz), 10.32 (d of d, 2 H, $J = 7$ Hz, 1 Hz), $3[SC_6H_4]_2$. $^{13}C\{^1H\}$ NMR: δ 7.5 (8 C, $2(CH_3CH_2)_4N$), 52.2 (8 C, $2(CH_3CH_2)_4N$), 123.2, 123.9, 124.8, 125.3, 125.8, 126.4, 129.2, 129.4, 129.8, 137.8 (2 C each, C_{arom}−H), 135.1 (4 C, C_{arom}−H), 143.0, 145.7, 145.8, 148.2, 149.0, 151.7 (2 C each, C_{arom}-no H). IR (Nujol, cm^{-1}): 3044 w $\nu(C{-}H_{arom})$; 1582 w; 1414 s; 1260 vw; 1170 w; 1112 vw; 1059 m; 1032 ms; 1001 w; 844 br w; 768 w; 746 s; 695 m; 667 w. UV−vis [CH_3CN; λ_{max} in nm (ϵ in M^{-1} cm^{-1})]: 256 (4.1×10^4), 324 (2.5×10^4), 402 (1.7×10^4). Anal. Calcd. for $C_{52}H_{64}N_2Ni_2S_6$: C, 60.82; H, 6.28; N, 2.73. Found: C, 61.05; H, 6.05; N, 2.53. Mp 175−177 °C (dec). CV: $E_{pa} = 1.10$, 0.06 V.

Synthesis of $[Et_4N]_2[NiL_2]$ (2). Na_2**L** was formed as described above for **1**, from H_2**L**[30] (0.389 g, 1.8 mmol) in 25 mL of THF, and then was

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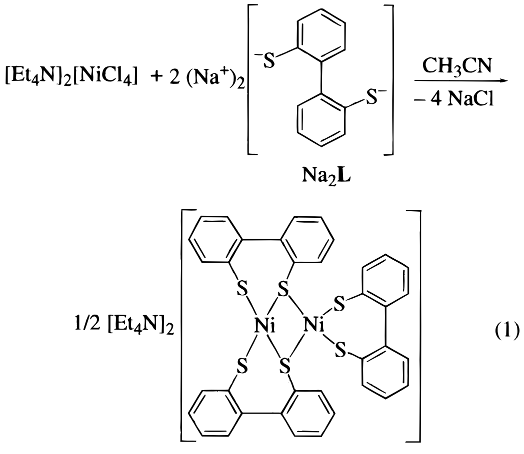
dissolved in CH_3CN (20 mL). To this solution $[Et_4N]_2[NiCl_4]$[29] (0.207 g, 0.45 mmol) in 25 mL of CH_3CN was added dropwise; the resulting green mixture was left to stir overnight. After filtration, 10 mL of C_6H_6 was added slowly. The resulting solution was cooled to ~5 °C overnight and then a white precipitate was filtered away. The addition of C_6H_6, cooling, and filtration steps were repeated two more times (10 mL, 60 mL). The solvent was removed, and 50 mL of Et_2O was added. After the mixture was stirred for 20 min the green solid was isolated by filtration and dried in vacuo overnight. Yield: 0.257 g (0.34 mmol, 77%). ^1H NMR: δ 1.29 (t, 24 H, $J = 7$ Hz, $2(CH_3CH_2)_4N$); 3.43 (q, 16 H, $J = 7$ Hz, $2(CH_3CH_2)_4N$), 6.67 (d of d, 4 H, $J = 7$, 1 Hz), 6.79 (~t of d, 4 H, $J = 7$ Hz, 1 Hz), 6.90 (~t of d, 4 H, $J = 7$ Hz, 1 Hz), 7.54 (d of d, 4 H, $J = 7$ Hz, 1 Hz), $2[SC_6H_4]_2$. $^{13}C\{^1H\}$ NMR: δ 7.5 (8 C, $2(CH_3CH_2)_4N$), 52.2 (8 C, $2(CH_3CH_2)_4N$), 122.8, 124.6, 129.0, 136.0 (4 C each, C_{arom}−H), 151.1, 152.0 (4 C each, C_{arom}-no H). UV−vis [CH_3CN; λ_{max} in nm (ϵ in M^{-1} cm^{-1})]: 259 (4×10^4), 378 (2×10^4). IR (Nujol, cm^{-1}): 3044 w $\nu(C-H_{arom})$; 1666 w; 1573 m; 1548 w; 1299 w; 1250 m; 1170 m; 1113 m; 1062 s; 1031 s; 847 m; 790 m; 749 s; 697 m; 665 m; 613 m. Mp 123−127 °C (dec). CV: $E_{pa} = 1.21$, −0.35 V.

Results and Discussion

The air-free addition of $(Et_4N)_2[NiCl_4]$[29] to 2−3 equiv of the disodium salt of the ligand[32] (Na_2**L**, made from 2,2′-dimercaptobiphenyl[30] and sodium metal) in acetonitrile (eq 1) forms the brown, dinuclear complex $[Ni_2L_3]^{2-}$ (**1**) as the tetraethylammonium salt. As expected for an anionic complex, $(Et_4N)_2$[**1**] is soluble in polar organic solvents such as acetonitrile, DMF, and DMSO and is insoluble in less polar solvents such as $CHCl_3$, THF, diethyl ether, and benzene. Complex **1** appears to be moderately stable to the air as a solid, but in solution the complex is sensitive to air, turning colorless over several hours, resulting in decomposition of the complex and formation of the ligand disulfide derivative. Complex **1** is slightly sensitive to water and protic solvents. Although **1** is stable in CH_3CN solution for at least an hour (by UV−vis spectroscopy), it will slowly decompose in dried solvents that it is soluble in, for instance, giving additional peaks of significant intensity in the ^1H NMR spectrum (d_7-DMF) after sitting overnight. The elemental analysis data fit the $(Et_4N)_2[Ni_2L_3]$ formulation.



Na_2**L**

1

(1)

Table 1. Selected Crystallographic Data for the Structures of **1** and **2**

parameter	$(Et_4N)_2$[**1**]·CH_3CN·$0.5Ph_2S_2$	$(Na^+·CH_3CN)(Et_4N)$[**2**]
empirical formula	$C_{60}H_{71}N_3Ni_2S_7$	$C_{34}H_{39}N_2NaNiS_4$
fw	1176.04	685.61
temp (K)	298	298
λ, Mo Kα (Å)	0.710 73	0.710 73
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	13.806(2)	9.9570(10)
b (Å)	14.267(2)	13.2670(10)
c (Å)	16.873(2)	13.9560(10)
α (deg)	69.263(10)	108.489(7)
β (deg)	69.267(8)	90.396(6)
γ (deg)	83.117(10)	103.570(4)
V (Å^3)	2906.9(7)	1693.0(2)
Z	2	2
calcd ρ (g/cm^3)	1.344	1.345
cryst size (mm)	0.60 × 0.20 × 0.04	0.70 × 0.38 × 0.21
μ (cm$^{-1)}$	9.40	8.59
$R1^a$	0.0752	0.0390
wR2^b	0.2011	0.0995

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ (observed data, $I > 2\sigma(I)$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ (all data).

Complex **1** is diamagnetic both in solution and in the solid state, as evidenced by sharp, unshifted ^1H and ^{13}C NMR spectra and a magnetic susceptibility measurement, respectively, consistent with a square planar geometry. There is, however, one aromatic peak with an unusual chemical shift, at 10.32 ppm, that is suggestive of deshielding via ring current effects and is consistent with a solution structure that places that particular proton in an environment near a phenyl ring a significant fraction of the time. The UV−vis spectrum of **1** is dominated by three intense peaks ranging from 256 to 402 nm in CH_3CN, some of which are reasonably assigned as ligand-to-metal charge transfer (LMCT) bands. A survey of a few square planar Ni−thiolate systems[33−41] shows a fairly broad range of UV−vis data reported for these complexes, with 2−5 peaks including λ_{max} values from 260 to 720 nm (nearly all of them quite intense, with ϵ values of at least 1500 M^{-1} cm^{-1}).

Fast evaporation of an acetonitrile solution of $(Et_4N)_2$[**1**] open to the air yielded single crystals containing not only the two Et_4N^+ counterions in the lattice but an acetonitrile molecule and half a molecule of biphenyl disulfide as well. The X-ray crystal structure (Table 1) confirmed the dinuclear $[Ni_2L_3]^{2-}$ formulation for **1** (Figure 1) and the square planar geometry about both Ni(II) ions. The S−Ni(1)−S angles average to 90.01° but range from 84.15 to 95.93°; for Ni(2) the average is 90.31°, although the range is greater, from 82.65 to 96.27°. Both nickel ions are essentially in the S_4 plane; Ni(1) is displaced by 0.001 Å and Ni(2) by 0.003 Å. The entire Ni_2S_6 portion of the

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(32) To our knowledge, the transition metal coordination chemistry of **L** is limited to a Ti(IV) complex (Stafford, P. R.; Rauchfuss, T. B.; Verma, A. K.; Wilson, S. R. *J. Organomet. Chem.* **1996**, *526*, 203−214) and a Mo(V) complex (Tipton, A. A.; Conry, R. R. Manuscript submitted).

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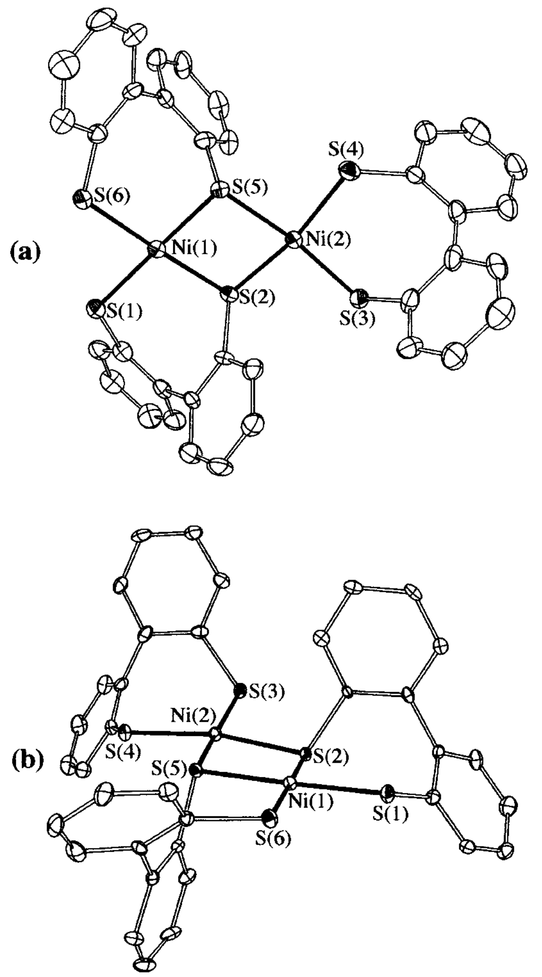

Figure 1. (a) Thermal ellipsoid plot of the solid-state structure of $[Ni_2\mathbf{L}_3]^{2-}$ (**1**) at the 25% probability level (hydrogen atoms omitted for clarity). (b) Different view of $[Ni_2\mathbf{L}_3]^{2-}$ at the 10% probability level. Selected bond distances (Å) and angles (deg) are the following: Ni(1)−S(1) 2.203(4); Ni(1)−S(2) 2.201(3); Ni(1)−S(5) 2.191(4); Ni(1)−S(6) 2.204(3); Ni(2)−S(2) 2.232(4); Ni(2)−S(3) 2.195(3); Ni(2)−S(4) 2.192(4); Ni(2)−S(5) 2.224(3); S(1)−Ni(1)−S(2) 95.93(13); S(1)−Ni(1)−S(6) 85.50(13); S(2)−Ni(1)−S(5) 84.15(12); S(5)−Ni(1)−S(6) 94.46(13); S(1)−Ni(1)−S(5) 178.24(14); S(2)−Ni(1)−S(6) 177.79(14); S(2)−Ni(2)−S(3) 93.01(13); S(3)−Ni(2)−S(4) 96.27(13); S(2)−Ni(2)−S(5) 82.65(12); S(4)−Ni(2)−S(5) 89.31(13); S(2)−Ni(2)−S(4) 167.95(13); S(3)−Ni(2)−S(5) 170.08(13).

molecule is not quite planar, having a small bend between the two $Ni-S_4$ planes, exhibiting an angle of 8.8°. This is also reflected in the fairly large $Ni-S_b-Ni$ angles (S_b and S_t = bridging and terminal thiolate sulfur atoms, respectively) of 96.12(13)° for S(2) and 96.64(14)° for S(5). The average Ni−S distances for the terminal and bridging thiolates in **1** are within error of one another, at 2.199 and 2.212 Å, respectively. However, there is a noticeable difference between those from Ni(1) and Ni(2); the terminal distances to Ni(2) are shorter and the bridging Ni(2)−S distances are longer than the corresponding Ni(1) distances. A long Ni(1)···Ni(2) separation of 3.298 Å suggests that there is no Ni−Ni interaction (the Ni−Ni distance is 2.50 Å in nickel metal).

The Ni−S distances and angles found for **1** are comparable to other square planar dinuclear Ni(II)−tetrathiolate complexes. Thus, for four structures of three such complexes,[34−36,39,42] the terminal thiolates were found between 2.162 and 2.219 Å and the bridging thiolates from 2.158 to 2.225 Å. Although terminal nickel−thiolate distances often appear to be slightly shorter than bridging nickel−thiolate distances, it seems that bridging nickel−thiolate distances vary over a broader range of values than terminal distances when many complexes are considered. However, these differences often end up being within the error of the experiment. For example, in a statistical study published in 1989, nickel−alkanethiolate complexes gave terminal Ni−S distances (8 complexes) averaging 2.187(7) Å and bridging Ni−S distances (16 complexes) averaging 2.201(24) Å.[43] The nickel−sulfur distances in the [NiFe]-ase and [NiFeSe]-H_2-ase structures appear to be a little longer than the distances in the model complexes, with averages for terminal $Ni-S_{cys}$ at 2.2−2.5 Å and bridging $Ni-S_{cys}$ at 2.4−2.6 Å. X-ray absorption spectroscopy suggests similar distances, typically in the 2.2−2.4 Å range.[44−46] The nickel−nickel distances in the small-molecule structures varied from 2.914 to 3.355 Å,[34−36,39,42] which appear to be longer than the nickel−iron distances found in the hydrogenase crystal structures (2.5−2.9 Å). The angles between bridging thiolate ligands ($\angle S_b-Ni-S_b$) are typically smaller (83.40° av for **1**, from 79.0 to 84.78° in the other complexes[34−36,39,42]) than the angles between terminal thiolates ($\angle S_t-Ni-S_t$ of 86.43−95.1° for the other complexes,[34−36,39,42] 90.89° av for **1**).

All the sulfur−sulfur contacts in **1** are greater than 3.1 Å except for the interligand distances for the two **L** on Ni(1), which are 2.992 Å for S(1)−S(6) and 2.943 Å for S(2)−S(5). This results in a visible compression in the coordination sphere of Ni(1) (Figure 1). Short S−S contacts have also been noticed between the bridging thiolate groups in $(MeN_4)_2[Ni_2(SEt)_6]$ (2.906 Å)[34] and $(Ph_4P)_2[Ni_2(SCH_2CH_2S)_3]$ (2.820 Å).[36] In other systems these short sulfur−sulfur distances are considered to be partial disulfide bonds, for instance, in molybdenum−thiolate chemistry.[47] However, the partial disulfide bond distances are clearly much longer than those found for full sulfur−sulfur bonds; e.g., the crystal structure of the disulfide form of **L** has a S−S bond distance of 2.0520(12) Å.[48] In one of the [NiFe]-H_2-ase crystal structures[24] there is a short sulfur−sulfur distance of 3.0 Å between the two bridging cysteine ligands. However, it is not necessarily representative of a partial S−S bond because the uncertainties in the distances in biological structures can be large. In addition, the presence of the two other bridging atoms may force the two sulfur ligands together, giving a steric rather than electronic reason for any short distance between the two bridging cysteine ligands.

Other Ni−arylthiolate structures have displayed an electronic preference for the nickel, sulfur, and aryl groups to be coplanar, which has been used to explain[39,49] why alkylthiolate complexes were typically found to be planar but unconstrained arylthiolate complexes were usually tetrahedral. For **L**, it is clear that the phenyl groups are bent away from the Ni−S vectors. This is

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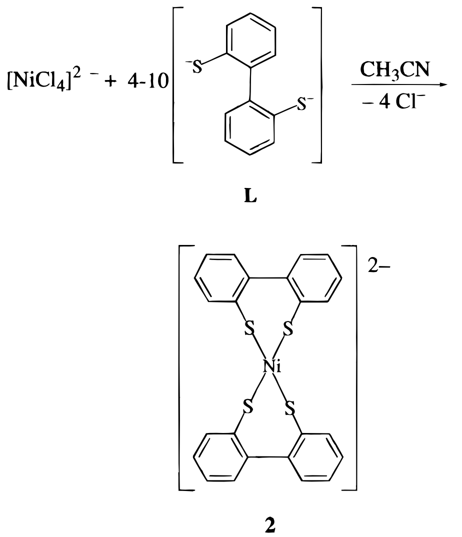
probably due to a greater tendency of the biphenyl groups to be canted (dihedral angles between the phenyl groups are 57.5, 54.3, and 54.8° for the ligands containing S(1,2), S(3,4), and S(5,6), respectively) instead of the geometry preference of the Ni(II) ion, which is not strong.[39,49]

If a larger excess of **L** is used in the reaction (e.g., from 4 to 10 equiv), a green complex (**2**) is formed instead of **1** (eq 2).



(2)

The solubility and air sensitivity of $(Et_4N)_2[\mathbf{2}]$ are similar to $(Et_4N)_2[\mathbf{1}]$. However, **2** is less stable both in solution and as a solid than **1** and seems to be more stable in the presence of excess **L** than without ligand. UV−vis spectra taken immediately of **2** in CH_3CN with and without excess **L** (~2 equiv Na_2**L**) are essentially the same. Without excess ligand, dissolution of **2** in solvent at room temperature results in a slow color change to the brown color characteristic of **1** over several days as peaks in the ^1H NMR spectrum due to **1** appear (a noticeable change in the UV−vis spectrum occurs within several hours; the decomposition of **2** is not significantly accelerated by the presence of MeOH). However, the addition of 2 equiv of Na_2**L** to **1** in CH_3CN does not give a UV−vis spectrum consistent with **2**.

Sharp, unshifted ^1H and ^{13}C NMR spectra again suggest a square planar geometry for the Ni(II) in complex **2** in solution. In addition, the presence of only six aromatic peaks in the ^{13}C NMR spectrum for **2** compared to three times as many for **1** suggests a higher molecular symmetry for **2** than **1** in solution and is consistent with the mononuclear $[Ni\mathbf{L}_2]^{2-}$ formulation. Integration of ^1H NMR spectra shows that the synthesis of **2** with four equiv of **L** forms the bis(tetraethylammonium) salt. The UV−vis spectrum of **2** contains two intense peaks at 259−378 nm in CH_3CN. Unfortunately, the extreme sensitivity of **2** toward the formation of **1** and the necessity of keeping **2** in the presence of excess **L** prevented complete purification and characterization of **2**, including the acquisition of acceptable elemental analysis data. This tendency of Ni(II)−thiolate complexes to polymerize is a well-known process[50] and is often attributed to a solvent-assisted dissociation equilibrium that promotes ligand loss, the presence of protons, or the method of synthesis and seems to depend on the system and conditions of isolation.[35,39,51−54] The synthesis of mononuclear Ni(II)−tetrathiolate complexes via the addition of a large excess of the ligand has been successfully used in other systems.[35,51,52]

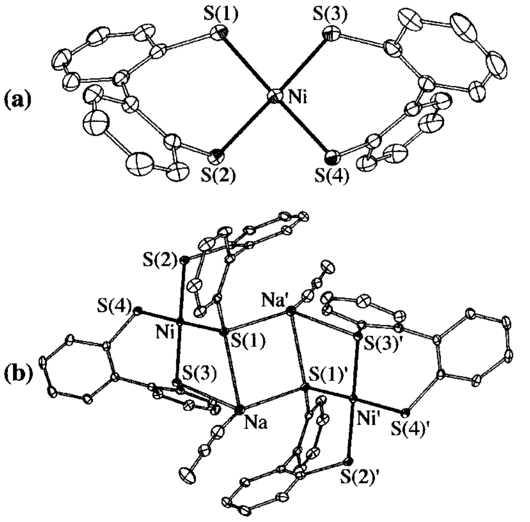


Figure 2. (a) Thermal ellipsoid plot of the solid-state structure of $[Ni\mathbf{L}_2]^{2-}$ (**2**) at the 25% probability level (hydrogen atoms omitted for clarity). (b) View at the 10% probability level of $[Ni_2Na_2(CH_3CN)_2\mathbf{L}_4]^{2-}$, which shows the sodium counterions bridging two mononuclear units. Selected bond distances (Å) and angles (deg) are the following: Ni−S(1) 2.2135(9); Ni−S(2) 2.2192(10); Ni−S(3) 2.2210(9); Ni−S(4) 2.2085(9); S(1)−Ni−S(2) 94.92(3); S(1)−Ni−S(3) 87.16(3); S(2)−Ni−S(4) 83.46(3); S(3)−Ni−S(4) 94.57(3); S(1)−Ni−S(4) 177.45(4); S(2)−Ni−S(3) 176.08(4).

Slow addition of diethyl ether to an acetonitrile solution of **2** synthesized with 10 equiv of Na_2**L** yielded several single, X-ray quality green crystals. The X-ray crystal structure (Table 1) established a mononuclear $[Ni\mathbf{L}_2]^{2-}$ formulation for **2** with square planar geometry about the Ni(II) ion (Figure 2a). The large excess of sodium ions compared to tetraethylammonium ions caused crystallization of **2** with one of each Et_4N^+ and Na^+ counterion. The mononuclear $[Ni\mathbf{L}_2]^{2-}$ fragment and a sodium counterion are sitting on a crystallographic inversion center. The result is a molecular solid-state structure containing two $[Ni\mathbf{L}_2]^{2-}$ fragments that are bridged by two sodium counterions that interact with the thiolate sulfurs of the two $[Ni\mathbf{L}_2]^{2-}$ cores (Figure 2b). The coordination sphere of each sodium ion is completed with an acetonitrile molecule.

The average Ni−S distance in the structure of **2** is 2.216 Å, with a range from 2.2085 to 2.2210 Å; there is no apparent influence of the long Na−S interactions (2.832 Å av) on the Ni−S distances or S−Ni−S angles. The nickel−sulfur distances in **2** are similar to those in **1** but are longer than most mononuclear square planar Ni(II)−thiolate complexes (2.156−2.212 Å),[38,52,55−60] which are frequently alkylthiolate-ligated or have bidentate arylthiolate ligands with planar constraints and/or five-membered chelate ring sizes (for example, benzene-1,2-

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dithiolate ligands). Mononuclear complexes with monodentate arylthiolate ligands typically display distorted tetrahedral structures.[49,51,61−63] The S−Ni−S angles in **2** average to 90.03° with the smallest at 83.46° and the largest at 94.92°. The individual S−Ni−S angles in **2** deviate more from 90° than nearly all of the other square planar $\mathrm{Ni^{II}}$−tetrathiolate complexes it can be compared to.[38,52,55−59] The interligand angles in **2** are smaller than the intraligand angles; a similar pattern is seen in **1** and probably reflects an influence of the bite angle of **L**. The nickel ion is slightly displaced out of the S_4 plane (Ni to S_4 plane distance 0.014 Å).

All of the intraligand S−S distances in **2** are greater than 3.2 Å. In contrast, the interligand distances are shorter: S(2,4) and S(1,3) at 2.947 and 3.057 Å. Only one of the other square planar Ni(II)−tetrathiolate complexes was found to have a S−S distance of less than 3.1 Å.[58] The dihedral angles for the biphenyl groups are 60.7 and 52.3° for the ligands containing S(1,2) and S(3,4), respectively. The distances between the metals are consistent with no interaction (Ni···Ni 6.815 and Na···Na 4.118 Å). The coordination sphere about the sodium ion appears to be quite distorted from tetrahedral perhaps because of an interaction with a phenyl ring from the neighboring Ni−tetrathiolate complex. In fact, there is a short contact between each $\mathrm{Na^+}$ and one of the 1-phenyl carbon atoms (distance 3.053 Å).

As is not unusual for Ni(II)−tetrathiolate complexes,[35,36,64] the cyclic voltammograms for **1** and **2** contain only irreversible oxidations, at 0.06 V (E_{pa} vs SCE) for **1** and −0.35 V for **2**. Square planar dinuclear complexes have had irreversible oxidations reported, for instance, for $[\mathrm{Ni_2(edt)_3}]^{2-}$ (edt = ethanedithiolate) at −0.21 V (E_{pa} vs SCE)[35] and at −0.32, −0.03, and +0.73 V (E_{pa} vs NHE).[36] Mononuclear Ni(II)−tetra(alkylthiolate) complexes exhibit more negative oxidations to Ni(III), typically quasireversible or reversible oxidations from −0.60 to −0.76 V in aprotic solvents.[38,52,58] In contrast, mononuclear Ni(II)−tetra(arylthiolate) complexes usually give irreversible oxidations in the −0.05 to −0.40 V (vs SCE) range.[64] For both **1** and **2** peaks assignable to the disulfide form[65] of **L** appear in the CVs. The appearance of peaks due to the disulfide form of **L** suggests that although oxidation first seems to occur at the nickel ion, ultimately the ligand is oxidized and is liberated. The ability to isolate the disulfide form of **L** from the reaction of either **1** or **2** with air supports this postulation.

Conclusions

Two new square planar Ni(II)−tetra(arylthiolate) complexes have been prepared and characterized. Although four-coordinate Ni(II)−thiolate complexes are predominately square planar in geometry, nearly all of the exceptions are mononuclear complexes with monodentate arylthiolate ligands that do not constrain the Ni ion to be square planar. The ligand **L**, with its seven-membered chelate ring size, has some flexibility to change its bite angle via the phenyl−phenyl bond and should not force a planar geometry on the complexes with **L** either. Therefore, it is interesting that **2** has adopted a square planar structure.

In the absence of excess **L** the mononuclear complex **2** readily loses a ligand to form the dinuclear complex **1**. In addition, oxidation by air causes complex decomposition, via ligand disulfide formation and dissociation, instead of oxidation at the thiolate ligand[66−68] or oxidation to Ni(III).[58] We are currently working to modify the ligand to inhibit disulfide formation and make the ligand more difficult to dissociate. We hope then to take advantage of the propensity of these complexes to pick up another metal ion on one side (e.g., another Ni(II) ion in **1** and a Na ion in **2**) to coordinate an iron center. The resulting heterodinuclear Ni/Fe cluster would more closely approximate the active sites found in the nickel−iron hydrogenases[24,25] so that relevant enzyme functional modeling studies can be carried out. Then, perhaps, results from this system could add to the already interesting results from and discussion of other relevant model complexes[69] as well as the recent discussions about possible modes of action of the enzyme[70−75] generated by the unanticipated findings from the crystal structures of the [NiFe]-$\mathrm{H_2}$-ases.

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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