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Discrete Mononuclear and Dinuclear Nickel(II) Complexes of Alkane- and Areneselenolates: Syntheses, Structures, and Properties of $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$, $(Ph_4P)_2[Ni(SePh)_4]$, and $(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]\cdot 8CH_3CN$

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Reaction of the alkanediselenolate $(Et_4N)_2(Se(CH_2)_3Se)$ with $NiCl_2\cdot 6H_2O$ in ethanol/acetonitrile mixture affords the dimeric complex $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (**1**), in which the coordination geometry around each Ni(II) center is square planar. In contrast, reaction of the areneselenolate $PhSe^-$ with $NiCl_2\cdot 6H_2O$ in acetonitrile gives rise to $(Ph_4P)_2[Ni(SePh)_4]$ (**2**), which comprises a distorted tetrahedral $NiSe_4$ chromophore. When the bulky areneselenolate $2,4,6\text{-}(Me)_3C_6H_2Se^-$ is used, the same reaction affords the dimeric complex $(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2\text{-}(2,4,6\text{-}(Me)_3C_6H_2Se)_4]\cdot 8CH_3CN$ (**3**), which contains square planar $NiSe_4$ chromophores. Unfavorable steric interactions among *o*-methyl groups, nickel, and the Se atoms do not allow a tetrahedral coordination sphere around nickel in **3**. Complex **1** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 16.645(3)$ Å, $b = 20.214(6)$ Å, $c = 11.428(3)$ Å, $V = 3846(3)$ Å^3, and $Z = 4$. The structure of **1** was refined to $R = 7.34\%$ on the basis of 1694 ($I > 4\sigma(I)$) data. Complex **2** crystallizes in the orthorhombic space group $Pca2_1$ with $a = 17.617(7)$ Å, $b = 13.758(5)$ Å, $c = 24.776(11)$ Å, $V = 6005(4)$ Å^3, and $Z = 4$. The structure of **2** was refined to $R = 6.45\%$ on the basis of 4034 ($I > 4\sigma(I)$) data. Complex **3** crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.443(3)$ Å, $b = 14.751(3)$ Å, $c = 15.351(3)$ Å, $\alpha = 75.66(3)°$, $\beta = 71.09(3)°$, $\gamma = 65.18(3)°$, $V = 2784.4(10)$ Å^3, and $Z = 1$. The structure of **3** was refined to $R = 7.34\%$ on the basis of 7236 ($I > 4\sigma(I)$) data. These Ni(II) selenolate complexes are sensitive to oxygen, and their formation is hindered by the presence of water in the reaction mixture. The average Ni−Se bond lengths in all the homoleptic square planar selenolates are shorter than the average Ni−Se bond length in the tetrahedral complex $[Ni(SePh)_4]^{2-}$.

Introduction

Spectroscopic studies have revealed a unique Ni−selenocysteine interaction at the active site of the [FeNiSe] hydrogenases.[1] X-ray Absorption Spectroscopy (XAS) indicates that the nickel site in the [FeNiSe] hydrogenases from *D. baculatus* is in a distorted trigonal bipyramidal (tbp) geometry with 3−4 N/O atoms at 2.06 Å, 1−2 S/Cl atoms at 2.1 Å, and 1 Se atom at 2.44 Å.[2] The catalytic properties of these enzymes are distinctly different from those of the [FeNi] hydrogenases, and the differences are believed to arise from the substitution of selenocysteine for cysteine at the nickel active site.[3] The recent finding that a UGA termination codon is used to direct the covalent insertion of selenocysteine into certain selenium-dependent enzymes strongly suggests that selenocysteine is indeed the twenty-first amino acid.[4] In addition, kinetic studies reveal a markedly higher rate of catalysis exhibited by the wild type selenocysteine-containing formate dehydrogenase as compared to the mutant cysteine-containing enzyme.[5] This information implies that the incorporation of selenium at the enzyme active site(s) is chemically advantageous and not merely the result of adaptation to selenium-rich environmental conditions.

In the last few years, a variety of metal selenolate complexes containing sterically demanding selenolate ligands and featuring different coordination numbers and geometries have been synthesized and structurally characterized.[6−14] These metal selenolates have important applications as precursors of semiconductors, superconductors, and photoconducting materials. While there are numerous compounds containing M−Se bonds,[6−17] examples of discrete nickel selenolates are still scarce.[18]

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In order to better understand the nature of Ni−Se interaction(s) at the biological nickel sites, we sought to develop the chemistry of selenolato complexes of nickel in different oxidation states. To date, we have synthesized two homoleptic mononuclear alkaneselenolates, $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2EtOH$ and $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$,[19] as well as several mixed-ligand selenolates, including $[Ni(terpy)(SePh)_2]_2$, $[Ni(dmp)(2,4,6\text{-}(Me)_3C_6H_2Se)_2]$, $[Ni(dmp)(SePh)_2]_2\cdot 2CH_3CN$, $[Ni(terpy)(2,4,6\text{-}(Me)_3C_6H_2Se)_2]$,[20] and [Ni(DAPA)(SePh)$_2$][21] (terpy = 2,2′,2′′-terpyridine, dmp = 2,9-dimethyl-1,10-phenanthroline, DAPA = 2,6-bis[1-(phenylimino)ethyl]pyridine). In this account, we report the syntheses, structures, and spectral properties of three homoleptic (two square planar and one tetrahedral) nickel selenolates, namely, $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (**1**), $(Ph_4P)_2[Ni(SePh)_4]$ (**2**), and $(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]\cdot 8CH_3CN$ (**3**).

Experimental Section

Preparation of Compounds. Potassium selenocyanate, 1,3-propanediyl dibromide, diphenyl diselenide, and selenophenol were procured from Aldrich Chemical Co. Bis(2,4,6-trimethylphenyl) diselenide was obtained from Lancaster. Freshly distilled and degassed solvents were used in all preparations. All manipulations were performed under an atmosphere of pure and dry dinitrogen using standard Schlenk line techniques.

1,3-Propanediyl Diselenocyanate ($NCSeCH_2CH_2CH_2SeCN$). The synthesis of 1,3-propanediyl diselenocyanate has been previously reported.[22] We have modified the synthetic procedure to some extent.

A 6.86 g (0.048 mol) sample of solid potassium selenocyanate was added to 45 mL of dry acetone in a 250 mL three-neck flask equipped with a magnetic stirrer and condenser. After the mixture had been heated to 40 °C, 4.43 g (0.022 mol) of 1,3-propanediyl dibromide was added dropwise via syringe to the solution with constant stirring. Within 5 min, a white solid appeared in the reaction mixture, which was stirred for 2 h at 50 °C. The mixture was then allowed to cool, and the potassium bromide that had formed was removed by filtration. Removal of acetone under reduced pressure resulted in an orange oily residue. The oil was then dissolved in minimum amount of diethyl ether, and the reaction flask was placed in an ice bath. The desired compound precipitated as white needles from this solution upon dropwise addition of water. The material was filtered from the solution in air, washed with small amounts of cold ether, and dried under vacuum. Yield: 2.65 g (48%). Mp = 52 °C. Selected IR bands (KBr pellet, cm^{-1}): 2955 (w), 2931 (w), 2861 (w), 2144 (vs), 1437 (s), 1420 (m), 1284 (m), 1232 (vs), 1208 (vs), 1167 (m), 1108 (s), 1044 (s), 814 (s), 744 (s), 515 (s). ^1H NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 2.32 (t, CH_2), 3.15 (t, CH_2). ^{13}C NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 38.1 (CH_2), 33.8 (CH_2), 110 (CN).

$(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (1). To a solution of 0.72 g (2.84 mmol) of 1,3-propanediyl diselenocyanate in 10 mL of ethanol at 0 °C was added, in small portions, 0.214 g (5.67 mmol) of $NaBH_4$. The addition took 40 min, after which the solution was stirred for an additional 1 h at 15 °C. Next, 0.92 g (5.55 mmol) of Et_4NCl was added and the ethanol removed under vacuum. The resultant $(Et_4N)_2(Se(CH_2)_3Se)$ was extracted into 25 mL of acetonitrile, whereupon a clear pale yellow solution was obtained. A batch of 0.133 g (0.56 mmol) of $NiCl_2\cdot 6H_2O$ was dissolved in 8 mL of ethanol, and the solution was slowly added to the selenolate solution. The dark orange-brown solution that resulted was stirred for 30 min. The volume of the reaction mixture was then reduced to 15 mL. Following addition of 5 mL of 2-propanol, the solution was kept at −20 °C for 10 h. Large dark brown blocks suitable for X-ray studies were obtained. Yield: 0.44 g (80%). Anal. Calcd for $C_{25}H_{58}N_2Se_6Ni_2$: C, 30.71; H, 5.98; N, 2.86. Found: C, 30.55; H, 5.90; N, 3.01. Selected IR bands (KBr pellet, cm^{-1}): 2966 (s), 2908 (s), 2814 (s), 1455 (vs), 1396 (s), 1279 (m), 1220 (m), 1179 (s), 1173 (s), 1032 (m), 1002 (s), 785 (m), 714 (w). ^1H NMR (300 MHz, CD_3CN, 298 K), δ (ppm from TMS): 1.08 (s, CH_2), 1.10 (s,CH_2), 1.29 (t, CH_3 of Et_4N), 1.73 (br, CH_2), 2.18 (d, CH_2), 3.34 (q, CH_2 of Et_4N). ^{13}C NMR (300 MHz, CD_3CN, 298 K), δ (ppm from TMS): 8.0 (Et_4N), 13.14 (CH_2), 16.7 (CH_2), 32.1 (CH_2), 32.5 (CH_2), 53.4 (Et_4N). Electronic absorption spectrum in DMSO, λ_{max} nm (ϵ, M^{-1} cm^{-1}) : 670 (sh, 785), 525 (3400), 343 (20 000), 290 (22 000).

$(Ph_4P)_2[Ni_2(Se(CH_2)_3Se)_3]$. This compound was prepared in the same manner as **1** except Ph_4PCl was used in place of Et_4NCl. No 2-propanol was used to precipitate the dark brown microcrystalline compound. Yield: 0.46 g (75%). Selected IR bands (KBr pellet, cm^{-1}): 3037 (w), 2966 (w), 2895 (w), 2814 (w), 1584 (w), 1478 (m), 1437 (s), 1314 (m), 1108 (s), 997 (s), 761 (m), 720 (s), 685 (s), 526 (s).

$(Ph_4P)_2[Ni(SePh)_4]$ (2). To a solution of 0.270 g (0.865 mmol) of diphenyl diselenide in 10 mL of ethanol was added 0.067 g (1.77 mmol) of $NaBH_4$, in small portions, and the temperature of the reaction mixture was kept at 0 °C. A batch of 0.287 g (1.73 mmol) of Et_4NCl was then added, and the ethanol was removed under vacuum. $(Et_4N)(SePh)$ was then extracted into 20 mL of acetonitrile (pale yellow solution). A suspension of $NiCl_2\cdot 6H_2O$ (0.075 g, 0.315 mmol) in 15 mL of acetonitrile was slowly added to this selenophenolate solution with constant stirring at 50 °C. During the addition, the color rapidly turned to dark brown. Next, a solution of 0.240 g (0.630 mmol) of Ph_4PCl in 5 mL of acetonitrile was added, and the mixture was stirred for 1 h. It was then concentrated to 25 mL. The desired complex separated from the mixture as a microcrystalline solid which was collected by filtration. The dark brown mother liquor afforded dark brown crystals of **2**, suitable for X-ray analysis, upon slow cooling at −20 °C. Combined yield: 0.38 g (90%). Anal. Calcd for $C_{72}H_{60}P_2Se_4Ni$: C, 63.51; H, 4.44. Found: C, 63.54; H, 4.53. Selected IR bands (KBr pellet, cm^{-1}): 3037 (w), 1584 (w), 1568 (s), 1484 (m), 1467 (s), 1431 (s), 1308 (m), 1102 (s), 1055 (s), 1020 (m), 997 (m), 756 (m), 744 (s), 720 (s), 685 (s), 662 (m), 521 (vs), 468 (m). ^1H NMR (500 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): −8.41 (*p*-H), 4.62 (*o*-H), 16.66 (*m*-H), 7.72−7.95 (Ph_4P^+).

$(Ph_4P)_2[Ni(SePh)_4]$ (**2**) was also synthesized using selenophenol. A solution of KSePh (prepared from 0.20 mL (1.88 mmol) of selenophenol and 0.104 g (1.85 mmol) of KOH in 15 mL of ethanol) was used. The final reaction mixture in acetonitrile was reduced in volume to 15 mL and cooled at −20 °C for 10 h. Yield: 0.3 g (65%).

$(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]\cdot 8CH_3CN$ (3). To a solution of 0.44 g (1.11 mmol) of bis(2,4,6-trimethylphenyl) diselenide in 15 mL of ethanol was added 0.086 g (2.28 mmol) of $NaBH_4$ in small amounts as the temperature of the reaction mixture was kept at 0 °C. A batch of 0.83 g (2.20 mmol) of Ph_4PCl was then added, and the ethanol was removed under vacuum. The resultant $(Ph_4P)(2,4,6\text{-}(Me)_3C_6H_2Se)$ was then extracted into 40 mL of acetonitrile (bright yellow-orange solution). A suspension of $NiCl_2\cdot 6H_2O$ (0.106 g, 0.44 mmol) in 15 mL of acetonitrile was slowly added to the selenolate solution with constant stirring at 50 °C, whereupon the color rapidly turned to dark brown. The mixture was stirred for 1 h and then filtered. The small amount of a dark purple-brown residue thus obtained was discarded. The mother liquor was kept at −20 °C for 10 h. Dark brown needles of **3** that formed during this period were filtered off and dried anaerobically. Yield: 0.20 g (45%). Anal. Calcd for $C_{118}H_{130}N_8P_2Se_6Ni_2$: C, 61.26; H, 5.66; N, 4.84. Found: C, 60.92; H, 5.34; N, 4.68. Selected IR bands (KBr pellet, cm^{-1}): 2966 (m), 2908 (m), 1584 (w), 1484 (w), 1455 (m), 1437 (s), 1367 (m), 1261 (m), 1108 (s), 1020 (m), 997 (m), 844 (m), 803 (m), 756 (m), 720 (s), 691 (s), 526 (vs).

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Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters

	complex **1**	complex **2**	complex **3**
formula (mol wt)	$C_{25}H_{58}N_2Se_6Ni_2$ (919.5)	$C_{72}H_{60}P_2Se_4Ni$ (1361.69)	$C_{118}H_{130}N_8P_2Se_6Ni_2$ (2313.42)
cryst color, habit	brown plate	brown needle	brown plate
cryst system	orthorhombic	orthorhombic	triclinic
space group	$Pna2_1$	$Pca2_1$	$P\bar{1}$
a, Å	16.645(3)	17.617(7)	14.443(3)
b, Å	20.214(6)	13.758(5)	14.751(3)
c, Å	11.428(3)	24.776(11)	15.351(3)
α, deg	90	90	75.66(3)
β, deg	90	90	71.09(3)
γ, deg	90	90	65.18(3)
V, Å^3	3846 (3)	6005 (4)	2784.4(10)
Z	4	4	1
d_{calcd}, g cm^{-3}	1.588	1.506	1.380
abs coeff μ, mm^{-1}	6.670	2.844	2.378
T, K	130	130	130
θ range, deg	0.0−22.50	1.48−22.50	1.41−22.52
R_1,[a] %	7.34	6.45	5.39
R_{2w}[b] (all independent data),[b] %	10.96	15.89	12.20
GOF[c]	0.66	1.049	1.027
largest diff peak and hole, e Å^{-3}	1.47, −0.92	1.45, −0.82	1.22, −0.75

[a] $R_1 = \sum||F_o| - F_c||/\sum|F_o|$. [b] $R_{2w} = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$. [c] GOF $= [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$where M = number of reflections and N = number of parameters refined.

$(Et_4N)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]$ was synthesized in an analogous manner except for the use of Et_4NCl instead of Ph_4PCl. Cooling of the mother liquor at −20 °C for 10 h afforded dark brown needles of $(Et_4N)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]$. Yield: 0.25 g (56%). Selected IR bands (KBr pellet, cm^{-1}): 2955 (m), 2908 (m), 1455 (vs), 1390 (m), 1367 (m), 1167 (m), 1014 (s), 844 (s), 779 (m), 726 (w), 544 (m).

Physical Measurements. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer, infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrometer, and NMR spectra were recorded on either a General Electric 300-MHz GN-300 or a Varian 500-MHz Unity Plus instrument.

X-ray Data Collection and Structure Solution and Refinement. Crystals for X-ray analysis were obtained by slow cooling of solutions of the respective complexes in acetonitrile. X-ray data were collected on a Siemens R3m/V diffractometer equipped with a graphite monochromator and an Enraf-Nonius low-temperature apparatus. Mo Kα (λ = 0.710 69 Å) radiation was employed. A mean fluctuation of 0.4% in the intensities of two standard reflections was observed during data collection for **1**. Only random fluctuations of <1.0% in the intensities of the two standard reflections were observed during the course of data collection for **2** and **3**. The structures of **1**−**3** were solved by direct methods.[23,24] For **1**, the space group was determined to be $Pna2_1$ (No. 33) or *Pnma* (No. 62) by the observation of systematic absences. Only $Pna2_1$ is a reasonable choice, since the molecule possesses neither mirror nor inversion symmetry. Accordingly, the structure was solved by direct methods in $Pna2_1$. The 1,3-propanediyl groups of the ligand and one of the two cations showed large thermal motions and hence were refined with restraints on the N-C and C−C distances and on the isotropic thermal parameters. Hydrogen atoms were not located in a difference map and were not included in the refinement. The handedness of the structure was determined by a SHELXTL routine.[23] For **2**, the structure was solved in the space group $Pca2_1$ (No. 29) using direct and difference Fourier methods. The alternative space group, *Pbcm* (No. 57), is not reasonable due to the lack of symmetry in the structure. Hydrogen atoms were added geometrically and refined with a riding model. In case of **3**, the asymmetric unit contains half of the complex anion, a molecule of PPh_4^+, and four molecules of acetonitrile. Two of the latter are somewhat disordered (exhibiting high thermal motion), but no model for the disorder could be constructed. Hydrogen atoms were added geometrically and refined with a riding model. In the final cycles of refinement, all non-hydrogen atoms except those of the above disorder were refined with anisotropic thermal parameters. The largest feature in the final difference map had a peak value of 1.22 e Å^{-3}, 1.3 Å from the acetonitrile with large thermal motion. For all three structures, refinements were performed by full-matrix least-squares methods and the data were corrected for absorption effects by use of the program XABS 2.[25] Machine parameters, crystal data, and data collection parameters are summarized in Table 1, and selected bond distances and angles are listed in Table 2. The remainder of the crystallographic data have been submitted as Supporting Information.

Results and Discussion

The dimeric complex $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (**1**) is formed in reactions of $NiCl_2\cdot 6H_2O$ with excess ligand in anhydrous acetonitrile/ethanol mixtures. All attempts to isolate the monomeric complex $[Ni(Se(CH_2)_3Se)_2]^{2-}$ with ligand:Ni ratios as high as 15:1 have failed so far. No solid material has been isolated from such reaction mixtures in the presence of cations like Et_4N^+. This is in contrast to the K^+ and Me_4N^+ salts of the monomeric selenolato complex $[Ni(SeCH_2CH_2Se)_2]^{2-}$, which are obtained in reactions of $NiCl_2\cdot 6H_2O$ with excess ligand (ligand:Ni = 5:1) in anhydrous ethanol.[19]

The Ph_4P^+ salts of the areneselenolato complexes $[Ni(SePh)_4]^{2-}$ (**2**) and $[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]^{2-}$ (**3**) are obtained in reactions of $NiCl_2\cdot 6H_2O$ with excess ligand (ligand:Ni = 5:1) in anhydrous acetonitrile. Although the ligand:Ni ratio of 5:1 is sufficient for the formation of the monomeric complex $(Ph_4P)_2[Ni(SePh)_4]$ (**2**), it is not enough in the case of $2,4,6\text{-}(Me)_3C_6H_2Se^-$ which affords only the dimeric complex $(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]$ (**3**). To date, there have been several attempts to synthesize the monomeric selenolato nickel complex with the 2,4,6-trimethylbenzeneselenolate ligand. In reactions of $2,4,6\text{-}(Me)_3C_6H_2Se^-$ with $NiCl_2\cdot 6H_2O$ (ligand:Ni = 5:1), the first visible product is a small amount of dark purple-brown insoluble material. The IR spectrum indicates that this material contains $2,4,6\text{-}(Me)_3C_6H_2Se^-$ but no Ph_4P^+ cation. It is quite possible that this material is $[Ni(2,4,6\text{-}(Me)_3C_6H_2Se)_2]_\infty$ although no attempt to confirm this notion has been made. The same reaction mixture, upon cooling, yields a second product which we have identified as $(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2\ Se)_4]$ (**3**). When this product is filtered off and the

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(23) Sheldrick, G. M. *SHELXTL PLUS: A Program for Crystal Structure Determination*, Version 4.2; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

(24) Scattering factors were taken from: *International Tables for Crystallography*; D. Reidel Publishing Co.: Boston, 1991; Vol. C.

(25) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

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

$(NEt_4)_2[Ni_2Se(CH_2)_3Se)_3]$ (**1**)			
Bond Lengths			
Ni(1)−Se(1)	2.287(5)	Ni(1)−Se(2)	2.275(5)
Ni(1)−Se(3)	2.342(6)	Ni(1)−Se(6)	2.351(3)
Ni(2)−Se(5)	2.327(5)	Ni(2)−Se(4)	2.325(8)
Ni(2)−Se(5)	2.297(6)	Ni(2)−Se(6)	2.279(7)
Se(1)−C(1)	2.00(4)	Se(4)−C(6)	2.02(4)
Se(3)−C(4)	1.99(3)	C(2)−C(3)	1.50(7)
C(1)−C(2)	1.49(6)	C(5)−C(6)	1.50(5)
Bond Angles			
Se(1)−Ni(1)−Se(2)	100.1(2)	Se(1)−Ni(1)−Se(3)	169.8(2)
Se(2)−Ni(1)−Se(3)	90.1(2)	Se(1)−Ni(1)−Se(6)	92.1(2)
Se(2)−Ni(1)−Se(6)	167.6(2)	Se(3)−Ni(1)−Se(6)	77.7(2)
Se(3)−Ni(2)−Se(4)	94.7(3)	Se(3)−Ni(2)−Se(5)	178.6(3)
Se(4)−Ni(2)−Se(5)	85.8(2)	Se(3)−Ni(2)−Se(6)	79.4(2)
Se(4)−Ni(2)−Se(6)	173.7(3)	Se(5)−Ni(2)−Se(6)	100.0(2)
Ni(1)−Se(1)−C(1)	114.8(11)	Ni(1)−Se(2)−C(3)	110.0(14)
Ni(1)−Se(3)−Ni(2)	83.0(2)	Ni(1)−Se(3)−C(4)	111.9(10)
Ni(2)−Se(3)−C(4)	104.8(10)	Se(1)−C(1)−C(2)	103(3)
C(1)−C(2)−C(3)	101(4)	C(4)−C(5)−C(6)	114(3)
$(PPh_4)_2[Ni(SePh)_4]$ (**2**)			
Bond Lengths			
Ni−Se(1)	2.386(3)	Ni−Se (2)	2.395(3)
Ni−Se(4)	2.403(3)	Ni−Se(3)	2.419(3)
Se(1)−C(1)	1.95(2)	Se(2)−C(7)	1.91(2)
Se(3)−C(13)	1.85(2)	Se(4)−C(19)	1.94(2)
C(2)−C(3)	1.38(3)	C(1)−C(2)	1.44(3)
P(1)−C(37)	1.78(2)	P(1)−C(25)	1.80(2)
P(2)−C(55)	1.80(2)	C(37)−C(38)	1.44(2)
Bond Angles			
Se(1)−Ni−Se(2)	94.37(11)	Se(1)−Ni−Se(4)	125.87(12)
Se(2)−Ni−Se(4)	117.39(12)	Se(1)−Ni−Se(4)	112.97(12)
Se(2)−Ni−Se(3)	117.66(12)	Se(4)−Ni−Se(3)	90.66(11)
C(1)−Se(1)−Ni	106.6(5)	C(7)−Se(2)−Ni	107.4(6)
C(13)−Se(3)−Ni	105.7(6)	C(19)−Se(4)−Ni	107.8(5)
C(6)−C(1)−C(2)	120(2)	C(6)−C(1)−Se(1)	118(2)
C(25)−P(1)−C(31)	109.3(8)	C(37)−P(1)−C(43)	111.1(8)
C(26)−C(25)−C(30)	120(2)	C(67)−P(2)−C(61)	110.0(8)
C(60)−C(55)−C(56)	120(2)	C(61)−P(2)−C(55)	107.6(8)
$(PPh_4)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]\cdot 8CH_3CN$ (**3**)			
Bond Lengths			
Ni−Se(3)	2.322(2)	Ni−Se (1)	2.326(2)
Ni−Se(2)	2.335(2)	Ni−Se (1)^{i}	2.355(2)
Se(1)−C(1)	1.940(7)	Se(1)−Ni^{i}	2.355(2)
Se(2)−C(10)	1.940(7)	Se(3)−C(19)	1.941(7)
C(1)−C(2)	1.402(10)	C(1)−C(6)	1.419(10)
C(4)−C(8)	1.507(10)	C(2)−C(7)	1.517(10)
C(6)−C(9)	1.483(10)	C(10)−C(11)	1.397(11)
C(10)−C(15)	1.390(11)	C(11)−C(18)	1.513(12)
C(13)−C(17)	1.541(11)	C(20)−C(25)	1.497(10)
C(34)−C(35)	1.385(11)	C(40)−C(41)	1.376(10)
P−C (40)	1.791(7)	P−C (46)	1.795(7)
Bond Angles			
Se(3)−Ni−Se(1)	96.09(5)	Se(3)−Ni−Se(2)	93.16(5)
Se(1)−Ni−Se(2)	170.73(5)	Se(3)−Ni−Se(1)^{i}	172.92(5)
Se(1)−Ni−Se(1)^{i}	82.79(5)	Se(2)−Ni−Se(1)^{i}	88.10(5)
C(1)−Se(1)−Ni	110.2(2)	C(1)−Se(1)−Ni^{i}	110.6(2)
Ni−Se(1)−Ni^{i}	97.21(5)	C(10)−Se(2)−Ni	111.7(2)
C(19)−Se(3)−Ni	110.9(2)	C(2)−C(1)−C(6)	120.4(7)
C(2)−C(1)−Se(1)	118.1(6)	C(6)−C(1)−Se(1)	121.3(5)
C(5)−C(4)−C(8)	120.3(7)	C(4)−C(5)−C(6)	123.0(7)
C(1)−C(6)−C(9)	122.8(7)	C(5)−C(6)−C(9)	119.8(7)
C(11)−C(10)−Se(2)	119.2(6)	C(10)−C(11)−C(16)	121.8(7)
C(12)−C(11)−C(16)	118.5(8)	C(21)−C(22)−C(26)	121.5(8)
C(28)−C(29)−C(30)	120.2(7)	C(35)−C(34)−C(39)	119.8(7)
C(28)−P−C(46)	108.6(4)	C(35)−C(34)−P	118.9(6)
C(39)−C(34)−P	121.3(6)	C(46)−P−C(34)	110.2(4)

[a] Symmetry transformation used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z$.

filtrate is concentrated, a small amount of a third product, an orange-brown microcrystalline material, is obtained.

The same three products are obtained when higher ligand:Ni ratios are employed (ligand:Ni = 8:1 and higher). In such cases, the first product is the insoluble purple-brown material and the second product is the crystalline $(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2\text{-}Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]$ (**3**). However, a much larger amount of the third product is obtained under these conditions. The large, clear, orange-brown crystals of the third product have been identified spectroscopically as the salt $[Ph_4P^+][2,4,6\text{-}(Me)_3C_6H_2Se^-]$ (^1H NMR (300 MHz, $(CD_3)_2SO$, 298 K), δ (ppm from TMS): 6.54 (2 *m*-H), 2.01 (*p*-CH_3), 2.24 (2 *o*-CH_3), 7.69−7.98 (Ph_4P^+)). The same three species are also obtained when Et_4N^+ is used as the cation.

It is now evident that the monomeric complex $[Ni(2,4,6\text{-}(Me)_3C_6H_2Se)_4]^{2-}$ is not formed because of steric reasons. The 2,4,6-trimethylbenzeneselenolate ligand has two methyl groups in the ortho positions on the phenyl ring. Both the X-ray structure and the CPK model of $[Ni(SePh)_4]^{2-}$ clearly indicate that the substitution of methyl groups for hydrogen atoms in the ortho positions on the phenyl rings leads to unusual steric crowding around the Ni−Se bonds. Such crowding hinders the formation of the corresponding monomeric complex $[Ni(2,4,6\text{-}(Me)_3C_6H_2Se)_4]^{2-}$. As a consequence, the dimeric complex **3** is formed under all experimental conditions. In the dimeric structure, the four terminal and two bridging selenolates are oriented in specific directions (vide infra, Figure 4) such that the methyl groups are apart from each other. Also, the Ni−Se distances of the two bridging selenolates are longer. Further discussions on this topic are included in the following sections.

Role of Water in the Reaction Mixtures. The homoleptic alkaneselenolates $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$, $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$,[19] and $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (**1**) are all synthesized in anhydrous ethanol or anhydrous ethanol/acetonitrile mixtures. Unlike the successful synthesis of the thiolate analogues in water,[27] the formation of the homoleptic selenolate complexes is impeded by the presence of small amounts of water in the reaction medium. In the case of $K_2[Ni(SeCH_2CH_2Se)_2]$, addition of ~10% water to the reaction mixture results in a brown solution from which no selenolate complex is obtained. Only small amounts of the brown crystalline selenide salt K_2Se_3 are isolated from such reaction mixtures.[19,28] The areneselenolates of nickel(II) are more sensitive to the presence of protic solvents and are not formed in the presence of >5% water (or any protic solvent). Thus, addition of ~10% water to the reaction mixture hinders the formation of the areneselenolates **2** and **3**; only insoluble materials are obtained in significant yields under such conditions. IR spectra indicate that the insoluble products are most likely $[Ni(SeC_6H_2R_3)_2]_\infty$ (R = H, Me).

Structure of $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (1). The crystal structure of **1** consists of discrete Et_4N^+ ions and the dimeric anion $[Ni_2(Se(CH_2)_3Se)_3]^{2-}$ (Figure 1). The coordination geometry of both nickel atoms in $[Ni_2(Se(CH_2)_3Se)_3]^{2-}$ is square

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(26) It is interesting to note that while the monomeric thiolato complex $[Ni(SCH_2CH_2S)_2]^{2-}$ is formed only in reaction mixtures with high ligand:Ni ratios (10:1),[27] the corresponding selenolato complex $[Ni(SeCH_2CH_2Se)_2]^{2-}$ does not require a high concentration of ligand in the reaction mixture; a ratio of ligand:Ni = 5:1 is sufficient for the successful isolation of $[Ni(SeCH_2CH_2Se)_2]^{2-}$.

(27) Baidya, N. B.; Stephan, D. W.; Campagna, C. F.; Mascharak, P. K. *Inorg. Chim. Acta* **1990**, *177*, 233.

(28) It appears that, in such reaction mixtures containing excess alkaneselenolates, cleavage of the C−Se bond occurs to some extent. Cleavage of C−Se bond is known to occur in other organic transformations. See: Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, U.K., 1986.

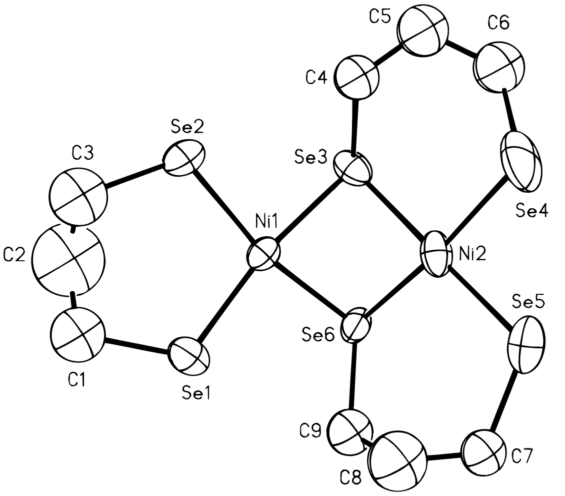

Figure 1. Thermal ellipsoid plot at the 50% probability level of the anion of **1** with the atom-labeling scheme. Hydrogen atoms are omitted for the sake of clarity.

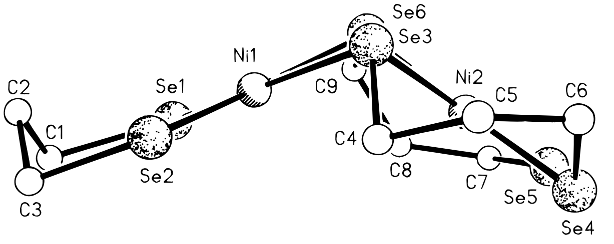

Figure 2. Computer-generated side view of the anion of **1** showing the square planar coordination of Se atoms around the two nickel centers.

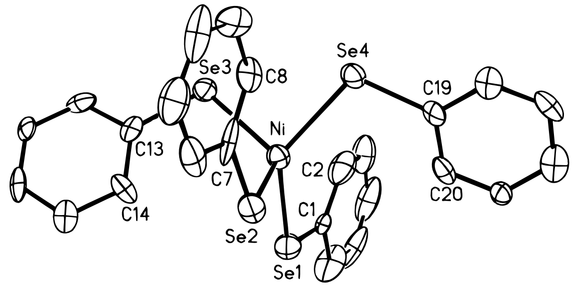

Figure 3. Thermal ellipsoid plot at the 50% probability level of the anion of **2** with the atom-labeling scheme. Hydrogen atoms are omitted for the sake of clarity.

planar. A side-on view of the complex anion depicts these two planar $NiSe_4$ cores (Figure 2). The average Ni−Se(terminal) and Ni−Se(bridging) bond distances are 2.296(5) and 2.324(5) Å, respectively (Table 2). These distances are slightly shorter and longer, respectively, than the average Ni−Se bond length of 2.305(3) Å in $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$.[19] The average Se−C bond length in **1** is very close to 2.0 Å.

$(Ph_4P)_2[Ni(SePh)_4]$ (2). Discrete Ph_4P^+ and $[Ni(SePh)_4]^{2-}$ ions are noted in the crystal structure of **2**; there are no unusual interactions between the cations and the complex anions in the solid state. The $NiSe_4$ core is of distorted tetrahedral geometry (Figure 3). The Ni−Se bond lengths range from 2.386(3) to 2.419(3) Å (average = 2.401(3) Å) (Table 2). The average Se−C distance is 1.91(2) Å. Homoleptic four-coordinate arenethiolato complexes of Ni (and Co, Zn, and Cd) are also of distorted tetrahedral geometry.[29] In these $[M(SAr)_4]^{2-}$ complexes, deviations from ideal tetrahedral geometry arise from the tendency of the Ni−S bonds to lie in the plane of the phenyl rings that are attached to the sulfur atoms.[29c] Unfavorable steric interactions between phenyl ortho hydrogen atoms and the nickel and sulfur atoms are also responsible for the observed distortions.[29b,c] The nonideal flattened tetrahedral geometry that exists in **2** presumably arises from the same tendency of the Ni−Se bonds to lie in the plane of the respective phenyl rings that are attached to the selenium atoms. Figure 3 depicts this as well as the fairly close proximity of the ortho hydrogen atoms to the central nickel atom.[30] The average Ni−Se bond length in **2** is 0.11 Å longer than the average Ni−S bond length in $[Ni(SPh)_4]^{2-}$ (2.288 Å).[29] This same difference of 0.11 Å has been seen for Fe, Zn, and Cd complexes of $[M(QPh_4]^{2-}$, where Q = Se or S.[31]

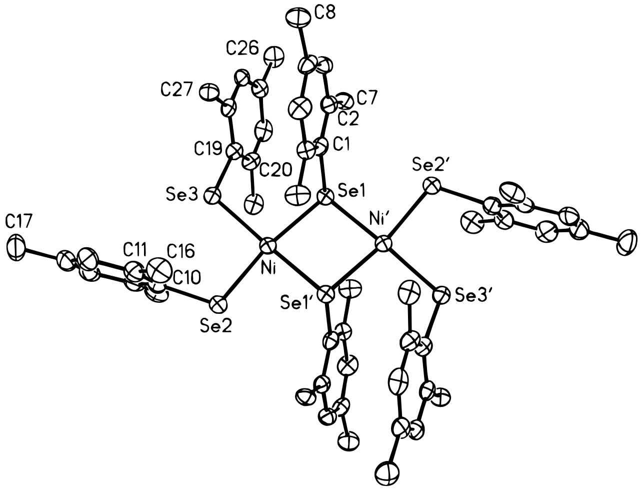

Figure 4. Thermal ellipsoid plot at the 50% probability level of the anion of **3** with the atom-labeling scheme. Hydrogen atoms are omitted for the sake of clarity.

While Ibers and co-workers had previously reported the syntheses of Ph_4P^+ and Et_4N^+ salts of $[M(SePh)_4]^{2-}$ (M = Mn, Fe, Co, Ni), only the iron complex was structurally characterized.[18a] The $FeSe_4$ core is only slightly distorted from ideal tetrahedral geometry compared to the $NiSe_4$ core in **2**, which is comparatively more flattened. The average Fe−Se bond length in $[Fe(SePh)_4]^{2-}$ is 2.460(12) Å, compared to 2.401(3) Å for $Ni-Se_{avg}$ in **2**. However, the average Se−C bond length in $[Fe(SePh)_4]^{2-}$ is 1.907 (8) Å, which is very close to $Se-C_{avg}$ in $[Ni(SePh)_4]^{2-}$.

$(Ph_4P)_2[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]\cdot 8CH_3CN$ (3). The crystal structure of **3** is composed of discrete Ph_4P^+ and $[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3SeC_6H_2\text{-}Se)_4)]^{2-}$ ions and acetonitrile molecules of crystallization; there are no unusual interactions between the cations and the anions in the solid state. The complex anion $[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2\text{-}Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4)]^{2-}$ has a center of inversion, and the Ni···Ni distance is 3.512 Å. The coordination geometry around each nickel is square planar (Figure 4), and the nickel atom is 0.06 Å away from the least-squares plane of the four seleniums bonded to it. In **3**, the average bond length of the four terminal selenolates is 2.329(2) Å, while the average of the two bridging selenolates is 2.341(2) Å (Table 2). Both these distances are shorter than the average Ni−Se bond length in the complex anion $[Ni(SePh)_4]^{2-}$ (**2**, $Ni-Se_{avg}$ = 2.401(3) Å). It thus appears that the tetrahedral geometry requires somewhat longer Ni−Se

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(29) (a) Dance, I. G. *Polyhedron* **1986**, *5*, 1037. (b) Rosenfield, S. G.; Armstrong, W. H.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 3014. (c) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1934.

(30) The shortest contacts are 2.93 Å for Ni···H(2), 2.99 Å for Ni···H(8), 2.87 Å for Ni···H(14), and 3.15 Å for Ni···H(20).

(31) The Ni−Se bond distances in the alkaneselenolato complex $[Ni(SeCH_2CH_2Se)_2]^{2-}$ are also 0.11 Å longer than the Ni−S bonds in $[Ni(SCH_2CH_2S)_2]^{2-}$.

bonds in order to relieve steric interactions between *o*-H atoms and nickel, a feature that is not operative in the square planar geometry presumably due to different orientations of the phenyl rings (Figure 4). The *o*-methyl hydrogens fill the space above and below the $NiSe_4$ plane (Figure S1, Supporting Information). The average Se−C bond length in **3** is 1.940(7) Å.

Properties of the Nickel(II) Selenolates. Crystals of the nickel(II) alkaneselenolates $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$, $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$, and $(Et_4N)_2[Ni_2(Se(CH_2)_3Se)_3]$ (**1**) are all very sensitive to oxygen and decompose rapidly when exposed to air. While $K_2[Ni(SeCH_2CH_2Se)_2]\cdot 2C_2H_5OH$ and $(Me_4N)_2[Ni(SeCH_2CH_2Se)_2]\cdot 1.2H_2O$ decompose rapidly in methanol and ethanol in the absence of excess ligand, **1** is more stable in alcohols; the clear orange-brown solutions can be stored for at least 1 h at room temperature.

Although crystals of the areneselenolates **2** and **3** are stable in air for several hours, they are very sensitive to oxygen in solutions. They are soluble in aprotic solvents like DMSO, DMF, and CH_3CN but are insoluble in methanol or ethanol. The electronic absorption spectrum of $[Ni(SePh)_4]^{2-}$ in DMSO exhibits only a shoulder at ∼490 nm while $[Ni_2(\mu\text{-}2,4,6\text{-}(Me)_3C_6H_2Se)_2(2,4,6\text{-}(Me)_3C_6H_2Se)_4]^{2-}$ displays a definite band with a maximum at 538 nm ($\epsilon = 6800\ M^{-1}\ cm^{-1}$).

The Alkane- and Areneselenolates of Ni(II): Relevance to [FeNiSe] Hydrogenases. Comparison of metric features of the structurally-characterized nickel(II) alkane- and areneselenolates reveals that the average Ni−Se distances in square planar complexes are shorter than those observed with the tetrahedral ones. The tetrahedral aryl complex **2** also exhibits the shortest average Se−C bond length (1.91 Å); average Se−C bond lengths of the alkaneselenolates $[Ni(SeCH_2CH_2Se)_2]^{2-}$ and $[Ni_2(Se(CH_2)_3Se)_3]^{2-}$ lie in the range 1.97−2.01 Å. EXAFS studies on the *D. baculatus* [FeNiSe] hydrogenase estimate the Ni−Se bond length at 2.44 Å. Since a selenocysteinate residue is coordinated to nickel at the enzyme active site, one can postulate that the discrepancy in Ni−Se distances between the nickel(II) alkaneselenolates and the biological nickel site (2.3 vs 2.44 Å) arises, at least in part, from lower active site symmetry presumably imposed by the protein framework. It is however important that this hypothesis is further supported by several other selenolate complexes, including ones containing selenocysteinate as ligands in different geometries. Research work in such direction is in progress in this laboratory.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: A computer-generated drawing of **3** showing methyl hydrogens filling space above and below the $NiSe_4$ planes (Figure S1) and crystal structure data for **1**−**3**, including atomic coordinates (Tables S1−S3), complete bond lengths (Tables S4−S6) and angles (Tables S7−S9), anisotropic thermal parameters (Tables S10−S12), and H atom coordinates (Tables S13−S15) (23 pages). Ordering information is given on any current masthead page.

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