

analysis, but the amplitude and degree of uniaxiality of libration can in principle be determined from the orientation dependence of T_1 and from the observed *effective* quadrupole coupling parameters as was done for calf thymus DNA.^{6,17} It would be particularly worthwhile to monitor the onset of large angle slow motion with increasing hydration of both polynucleotides via spin-alignment echo decays¹⁸ or hole-burning experiments.^{19,20}

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Registry No. Poly(A)-poly(u), 24936-38-7; poly(I)-poly(C), 24939-03-5; poly(G)-poly(C), 25280-45-9.

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Synthesis, Structure, and Characterization of a Mixed-Valence [Ni(II)Ni(III)] Thiolate Dimer

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Stable Ni(III) thiolate compounds as models for the Ni(III)-cysteine center in hydrogenase enzymes continue to be of interest.¹ Attention has been drawn to the unusual properties of the nickel-containing hydrogenase enzymes.² In particular, these hydrogenase enzymes contain a stable Ni(III) center that exhibits a Ni(III)/Ni(II) redox couple between -0.390 and -0.640 V vs SCE.² Spectroscopic evidence suggests that the coordination environment about the nickel contains three or four sulfur ligands in a distorted octahedral or square pyramidal array.³ In the quest for reasonable models for the nickel center in hydrogenases, it seemed that the ligand, $[P(o-C_6H_4S)_3]^{3-}$,⁴⁻⁶ might provide a suitable coordination environment for the nickel. DeVries and Davison have shown that $[P(o-C_6H_4S)_3]^{3-}$ coordinates to Tc(III) to provide five- or six-coordinate complexes of the formulation $[Tc[P(o-C_6H_4S)_3](CNR)_n]$ ($n = 1$ or 2).⁵ We report that the reaction of $[P(o-C_6H_4S)_3]^{3-}$ with Ni(II) yields a dimeric product, $[Ni_2[P(o-C_6H_4S)_3]_2]^{2-}$, that can be oxidized by two consecutive one-electron processes to give the stable $[Ni(III)Ni(II)]$ and $[Ni(III)Ni(III)]$ species, respectively.

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(4) Abbreviations: $P(o-C_6H_4SH)_3$ = tris(2-mercaptophenyl)phosphine; $P(o-C_6H_4SH)_2(Ph)$ = bis(2-mercaptophenyl)phenylphosphine; 2- PhC_6H_4SH = 2-phenylbenzenethiol.

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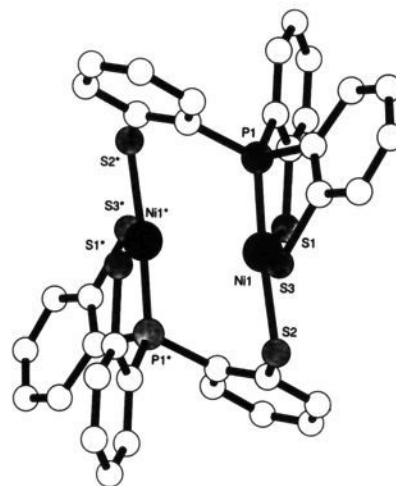


Figure 1. Structural diagram of $[Ni_2[P(o-C_6H_4S)_3]_2]^{2-}$. Selected bond distances (Å) and angles (deg): Ni1-S1 2.174 (4), Ni1-S2 2.233 (4), Ni1-S3 2.219 (5), Ni1-P1 2.109 (4); P1-Ni1-S1 89.2 (2), P1-Ni1-S2 171.8 (2), P1-Ni1-S3 84.6 (2), S1-Ni1-S2 96.7 (2), S1-Ni1-S3 156.0 (2), S2-Ni1-S3 87.8 (2).

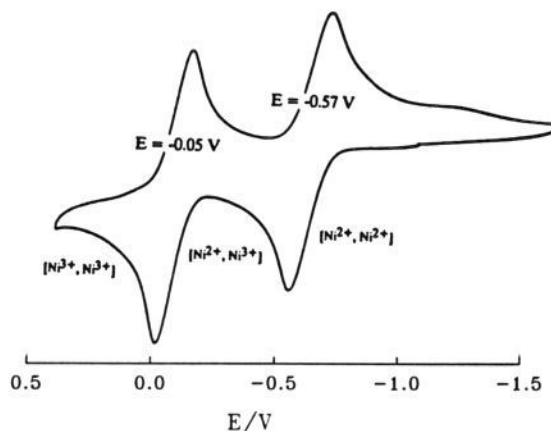


Figure 2. Cyclic voltammetric response (200 mV/s) of $[Pr_4N]_2[Ni_2[P(o-C_6H_4S)_3]_2]$ (**1**) in DMF with the indicated peak potentials vs SCE.

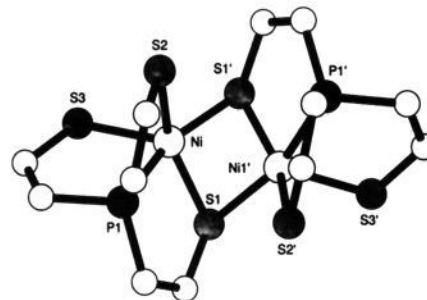


Figure 3. Structural diagram of the core of the $[Ni_2[P(o-C_6H_4S)_3]_2]^{2-}$ anion (parts of the phenyl rings have been omitted for clarity). Selected bond distances (Å) and angles (deg): Ni-Ni' 2.501 (2), Ni-S1 2.251 (2), Ni-S2 2.238 (2), Ni-S3 2.373 (2), Ni-P1 2.114 (2), Ni-S1' 2.260 (2), S1-Ni-S1' 82.13 (9), S1-Ni-S2 153.71 (8), S1-Ni-S3 105.49 (8), S1-Ni-P1 88.17 (7), S1'-Ni-P1 163.78 (8), S2-Ni-S3 99.62 (8), S2-Ni-P1 84.09 (7), S3-Ni-P1 90.07 (7), Ni-S1-Ni' 67.32 (7).

The reaction of $[P(o-C_6H_4SLi)_3]$ with 1 equiv of $Ni(acac)_2$ and $[(n-Bu)_4N]Br$ in methanol gives $[(n-Bu)_4N]_2[Ni_2[P(o-C_6H_4S)_3]_2]$ (**1**) in 72% yield. The X-ray structure of **1** is shown in Figure 1.⁷ The dianion, $[Ni_2[P(o-C_6H_4S)_3]_2]^{2-}$, which has crystallographic

(7) Crystal data for $1 \cdot 2CH_3OH$: $Ni_2S_6P_2O_2N_2C_{70}H_{104}$, monoclinic, $P2_1/c$, $a = 11.777$ (5) Å, $b = 19.421$ (7) Å, $c = 16.911$ (5) Å, $\beta = 99.95$ (4)°, $V = 3810$ (5) Å³, $Z = 2$. A total of 1809 unique reflections with $I > 3\sigma(I)$ were refined to $R = 0.065$ and $R_w = 0.065$.

C_2 symmetry, contains two parallel, distorted square planar $[\text{NiS}_3\text{P}]$ units linked together by the arms of the ligands. Each nickel is coordinated by two sulfurs and a phosphorus from one ligand and a sulfur from the other ligand to form a distorted square planar $[\text{NiS}_3\text{P}]$ array with the trans S1-Ni-S3 and P1-Ni-S2 angles being $156.0 (2)^\circ$ and $171.8 (2)^\circ$, respectively. The two $[\text{NiS}_3\text{P}]$ units are aligned on top of one another in an eclipsed configuration in which the nickel atoms are separated by a Ni1-Ni1' distance of $3.035 (4) \text{ \AA}$.⁸

Electrochemical studies⁹ indicate that $[\text{Pr}_4\text{N}]_2[\text{Ni}_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2$ (**1**) is oxidized by one electron to a $[\text{Ni}(\text{II})\text{Ni}(\text{III})]$ species at -0.57 V and then to a $[\text{Ni}(\text{III})\text{Ni}(\text{III})]$ species at -0.05 V (vs SCE) (Figure 2). Controlled potential electrolysis studies show both the $[\text{Ni}(\text{II})\text{Ni}(\text{III})]$ and $[\text{Ni}(\text{III})\text{Ni}(\text{III})]$ dimers to be thermally stable. $[\text{Ni}_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2^{2-}$ can be oxidized in situ or from isolated **1** by the addition of $[\text{Cp}_2\text{Fe}]\text{BF}_4$ to yield the mixed-valence $[\text{Ni}(\text{II})\text{Ni}(\text{III})]$ complex, $[\text{Pr}_4\text{N}][\text{Ni}_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2$ (**2**), in good yield.

The X-ray structure determination¹⁰ of **2** (Figure 3) illustrates that the $[\text{Ni}(\text{II})\text{Ni}(\text{II})]$ dimer has undergone a substantial structural change upon oxidation to the $[\text{Ni}(\text{III})\text{Ni}(\text{II})]$ species. The $[\text{Ni}_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2^{2-}$ anion has a crystallographically imposed C_2 axis centered between the two $[\text{NiS}_3\text{P}]$ square pyramidal units which are bridged by the S1 and S1' sulfur atoms. The structural transformation from **1** to **2** is accomplished by a twisting motion about the Ni-Ni axis with the two unique thiolates in **1** (S2 and S2') moving into the μ_2 bridging positions. Associated with this structural change is a 0.53 \AA shortening in the Ni-Ni distance to a value of $2.501 (2) \text{ \AA}$, which could be indicative of a substantial Ni-Ni interaction.^{8b} The structural change must be rapid on the time scale of the electrochemical measurements; the cyclic voltammogram of isolated **2** in DMF is completely analogous to that of **1**.^{9,11} The crystallographic symmetry that relates the two nickel centers in **2** rules out a type I (trapped-valence) electron configuration.¹²

In addition to the crystallographic evidence, the electronic spectrum of compound **2** suggests a delocalized mixed-valence state. Compound **2** absorbs more strongly in the visible region than does **1**, and it also exhibits two bands (lacking in **1**) of medium intensity in the near-IR region at 920 and 1325 nm.¹³ If the 920 and 1325 nm bands are assigned as intervalence transitions (IT), their broad band widths of the order 50 000–30 000 cm^{-1} along with their solvent dependence¹⁴ are suggestive of a class II mixed-valence species.^{12,15} Compound **2** gives a rhombic EPR spectrum (DMF/ CH_2Cl_2 glass at 100 K) with $g_x = 2.12$, $g_y = 2.09$, and $g_z = 2.03$.

The results described above are consistent with the observation that thiolates can stabilize the Ni(III) oxidation level at biologically relevant redox potentials.^{1a} Moreover, it is apparent that the chelating ability of the ligand has a marked effect upon the stability of the Ni(III)-thiolate center. We have synthesized and characterized a molecule that represents half the $[\text{Ni}_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2^{2-}$ dimer. That molecule which contains the $[\text{Ni}^{\text{II}}\text{S}_3\text{P}]$ core, $[\text{Et}_4\text{N}][\text{Ni}(\text{2-PhC}_6\text{H}_4\text{S})\text{Ni}(\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_2(\text{Ph}))]$ (**3**),¹⁶ cannot be

oxidized to a stable Ni(III)-thiolate species and in fact shows an irreversible CV wave at a potential of about -0.25 V (vs SCE), a result that is consistent with the work reported by others.¹⁷ These results can be extrapolated to indicate that the chelating nature of the hydrogenase proteins may be significant in stabilizing its $[\text{Ni}^{\text{III}}\text{-S-Cys}]$ center.

Compound **2** is unique because it is a crystallographically characterized mixed-valence nickel thiolate compound, as well as a robust Ni(III)-thiolate system.¹⁸ Also, further work has shown that the properties of the $[\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2^{3-}$ ligand can be exploited to prepare other mixed-valence complexes of the type described above, including $[\text{M}_2\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]_2^-$ ($\text{M} = \text{Co}$ and Fe).¹⁹

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Supplementary Material Available: Tables of crystallographic parameters, atomic coordinates, thermal parameters, bond distances and angles, and ORTEP diagrams for **1**–**3** (35 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

(16) Crystal data for **3**-CH₃OH: $\text{NiS}_2\text{PNC}_9\text{OH}_{46}$, monoclinic, $P2_1$; $a = 9.701 (4) \text{ \AA}$, $b = 20.247 (6) \text{ \AA}$, $c = 10.424 (4) \text{ \AA}$, $\beta = 114.52 (3)^\circ$, $V = 1863 (2) \text{ \AA}^3$, $Z = 2$. A total of 2616 reflections with $I > 3\sigma(I)$ were refined to $R (R_w) = 0.044 (0.058)$. The methylene groups of the cation are disordered. Selected bond distances (\AA) and angles (deg): Ni-S1 2.177 (2), Ni-S2 2.180 (2), Ni-S3 2.215 (2), Ni-P1 2.115 (2); S1-Ni-S2 166.1 (9), S1-Ni-S3 98.48 (9), S1-Ni-P1 87.65 (8), S2-Ni-S3 86.91 (9), S2-Ni-P1 87.65 (9), P1-Ni-S4 173.4 (1).

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Vesicle of a Hybrid Bolaamphiphile: Flip-Flop Behavior of Spin Labels

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Vesicle monolayers formed by hydrocarbon bolaamphiphiles, single hydrophobic chains with two polar groups, one at each end, provide a lot more intriguing properties than the usual bilayer membranes.¹⁻⁴ Fluorocarbon amphiphiles possess many peculiar characteristics, such as limited miscibility with hydrocarbon amphiphiles.⁵⁻¹⁰ In this communication, we report the synthesis of a single-chain hybrid bolaamphiphile with nearly equal lengths

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(9) Electrochemical studies: Solutions were 0.001 M in DMF with 0.1 M supporting electrolyte $[\text{Bu}_4\text{N}][\text{BF}_4]$; scan rate was 200 mV/s, referenced to the saturated calomel electrode (SCE). Compound **1** (Pt electrode) shows two one-electron oxidations ($E_{\text{ox}} + E_{\text{red}}/2 = E_{1/2}(\Delta E_p, i_{\text{pa}}/i_{\text{pc}})$) at -0.57 V (100 mV, 1.02) and -0.05 V (60 mV, 0.98). Compound **2** (glassy carbon electrode) shows a one-electron reduction at -0.50 V (130 mV, 0.92) and a one-electron oxidation at 0.05 V (90 mV, 0.94).

(10) Crystal data for **2**-2CH₃OH: $\text{Ni}_2\text{S}_6\text{P}_2\text{O}_7\text{NC}_{50}\text{H}_{60}$, monoclinic, $C2/c$; $a = 13.843 (1) \text{ \AA}$, $b = 17.487 (2) \text{ \AA}$, $c = 21.224 (3) \text{ \AA}$, $\beta = 94.26 (1)^\circ$, $V = 5124 (2) \text{ \AA}^3$, $Z = 4$. A total of 2549 unique reflections with $I > 3\sigma(I)$ were refined to $R = 0.052$ and $R_w = 0.069$. The cation is disordered.

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