5408 *Inorg. Chem.* **1996,** *35,* 5408−5409

A Homoleptic Thioether Coordination Sphere That Supports Nickel(I)

Pinghua Ge,[†] Charles G. Riordan,*[,†] Glenn P. A. Yap,[‡] and Arnold L. Rheingold[‡]

Departments of Chemistry, Kansas State University, Manhattan, Kansas 66506, and University of Delaware, Newark, Delaware 19716

Received May 9, 1996

Certain hydrogenases ([NiFe]H_2ase) and carbon monoxide dehydrogenase (CODH) are nickel-containing enzymes found in methanogenic, sulfate-reducing, and acetogenic bacteria that catalyze the oxidation of H_2, reduction of H^+ and CO oxidation, acetyl-CoA synthesis, respectively.[1] While the designed role for each is distinct, the primary coordination sphere about Ni in each is predominantly (or solely) sulfur ligation. The structure of the [NiFe]H_2ase from *Desulfovibrio gigas*, recently determined by X-ray methods, revealed the Ni to be coordinated to four cysteines in a distorted geometry.[2] In CODH, there are two catalytically distinct, yet structurally similar, Ni sites, clusters A and C, in which the average Ni environment as deduced from Ni EXAFS is S_4 or $N(O)_{2-3}S_2$.[3] Our current mechanistic understanding of these enzymes suggests that during catalysis the Ni cycles through the Ni(I) oxidation state.[1] The reduction from Ni(II) occurs at $E_{1/2} = -235$ mV for [NiFe]H_2ase (Ni−C) and at $E_{1/2} = -541$ mV for CODH (NiFeC).[4] While low molecular weight complexes have modeled the Ni(II/III) redox couple in an S-only environment, to our knowledge there is no example of a homoleptic $Ni^{II}S_x$ system that yields a stable $Ni^{I}S_x$ homologue upon chemical reduction.[5,6] Our understanding of these nickel-containing metalloenzymes would be greatly enhanced by the synthesis and characterization of model complexes that stabilize the +1 oxidation state in a sulfur-only ligation sphere. This account details our successful efforts toward stabilizing Ni(I) in such a coordination environment using poly((methylthio)methyl)borates as monoanionic chelates.[7]

Reaction of 2 equiv of $[Bu_4N]Ph_2Bt$[8] with $Ni(BF_4)_2\cdot 6H_2O$ in acetone resulted in precipitation of a deep red solid, $[Ph_2Bt]_2Ni$, **1**, in 55% yield, eq 1. Electronic and ^1H NMR

$$2[Bu_4N][Ph_2Bt] + Ni(BF_4)_2\cdot 6H_2O \rightarrow \underset{\mathbf{1}}{[Ph_2Bt]_2Ni} + 2[Bu_4N][BF_4] \quad (1)$$

spectroscopies[9] were consistent with a square planar structure ($S = 0$), which was confirmed by X-ray diffraction.[10] The molecular structure of **1** is depicted in Figure 1. The Ni ion resides on a crystallographic inversion center which renders *trans* thioethers metrically equivalent and ensures a planar ligation sphere. The Ni−S distances of 2.200(1) and 2.240(1) Å are similar to the $Ni-S_{eq}$ distance observed in the *D. gigas* [NiFe]H_2ase structure (average of 3 $Ni-S_{eq} = 2.25$ Å, $Ni-S_{ax} = 2.6$ Å)[2] and in one of the Ni EXAFS studies on CODH (2.23 Å).[3] The bond lengths are also consistent with other Ni(II)−S(thioether) distances in square planar geometries and are *ca.* 0.1 Å longer than Ni(II)−S(thiolate) bond lengths.[11] The bite angle of the borate chelate is slightly less than ideal: $\angle S(1)-Ni-S(2) = 86.31(4)°$. The six-membered chelate ring resides in a twisted-boat conformation which orients one of the CH_3 groups (C(15)) essentially perpendicular to the S_4 plane (displacement from S_4 plane 1.66 Å) while the other (C(16)) lies nearly in the S_4 plane (displacement from S_4 plane 0.11 Å). This disposition of the chelate places the phenyl substituents in distinct positions. One (Ph_{eq}) is directed away from the Ni, while the other (Ph_{ax}) is located directly above the NiS_4 plane. This latter orientation results in phenyl canopies protecting the open axial coordination sites with the Ph_{ax} centroid−Ni distance equal to 3.79 Å. A similar placement of pseudoaxial Ph groups

---

* To whom correspondence should be addressed. E-mail: Riordan@ksu.ksu.edu.

[†] Kansas State University.

[‡] University of Delaware.

(1) (a) Ragsdale, S. W. *Crit. Rev. Biochem. Mol. Biol.* **1991**, *26*, 261−300. (b) Lancaster, J. R., Ed. *The Bioinorganic Chemistry of Nickel*; VCH Publishers: New York, 1988; Chapters 8−10.

(2) Volbeda, A.; Charon, M.-H.; Piras, C.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *Nature* **1995**, *373*, 580−587. The authors describe the Ni coordination sphere as neither square planar nor tetrahedral.

(3) (a) Cramer, S. P.; Pan, W.-H.; Eidness, M. K.; Morton, T.; Ragsdale, S. W.; Der Vartanian, D. V.; Ljungdahl, L. G.; Scott, R. A. *Inorg. Chem.* **1987**, *26*, 2477−2479. (b) Bastian, N. R.; Diekert, G.; Niederhoffer, E. C.; Teo, B.-K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 5581−5582. (c) Xia, J.; Dong, J.; Wang, S.; Scott, R. A.; Lindahl, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 7065−7070.

(4) For potentials vs NHE, see for example: (a) Coremans, J. M. C. C.; van der Zwaan, J. W.; Albracht, S. P. J. *Biochim. Biophys. Acta* **1989**, *997*, 256−267. (b) Gorst, C. M.; Ragsdale, S. W. *J. Biol. Chem.* **1991**, *266*, 20687−20693.

(5) For an example of a $Ni^{II}S_4$ complex which is stable to *electrochemical* reduction, see: Yamamura, T.; Sakurai, S.; Arai, H.; Miyamae, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1656−1658.

(6) For examples of Ni(I) complexes with other chromophores see the following. $Ni^{I}N_4$: (a) Ram, M. S.; Riordan, C. G.; Ostrander, R.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 5884−5892. (b) Szalda, D. J.; Fujita, E.; Sanzenbacher, R.; Paulus, H.; Elias, H. *Inorg. Chem.* **1994**, *33*, 5855−5863. (c) Suh, M. P.; Kang, S.; Goedken, V. L.; Park, S. *Inorg. Chem.* **1991**, *30*, 360−365. (d) Lahiri, G. K.; Schussel, L. J.; Stolzenberg, A. M. *Inorg. Chem.* **1992**, *31*, 4991−5000. $Ni^{I}S_3N_2$: (e) Marganian, C. A.; Vazir, H.; Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1995**, *117*, 1584−1594. (f) Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1991**, *30*, 929−937. $Ni^{I}N_2S_2$: (g) Farmer, P. J.; Reibenspies, J. H.; Lindahl, P. A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1993**, *115*, 4665−4674. $Ni^{I}NS_3C$: (h) Stavropoulos, P.; Muetterties, M. C.; Carrié, M.; Holm, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 8485−8492. $Ni^{I}N_5$: (i) Suh, M. P.; Oh, K. Y.; Lee, J. W.; Bae, Y. Y. *J. Am. Chem. Soc.* **1996**, *118*, 777−783.

(7) (a) Ge, P.; Haggerty, B.; Rheingold, A. L.; Riordan, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 8406−8407. (b) Ohrenberg, C.; Ge, P.; Schebler, P.; Riordan, C. G.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 749−754. (c) Ohrenberg, C.; Saleem, M. M.; Riordan, C. G.; Yap, G. P. A.; Verma, A. K.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1996**, 1081−1082.

(8) Abbreviations: Ph_2Bt^-, diphenylbis((methylthio)methyl)borate; [14]-aneS_4, 1,4,8,11-tetrathiacyclotetradecane; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

(9) ^1H NMR ($CDCl_3$, 27 °C): δ 7.26 (br, *o-H*, 8 H), 7.20 (t, *m-H*, 8 H), 7.06 (t, *p-H*, 4 H), 1.82 (s, CH_3SCH_2, 20 H). UV−vis (CH_2Cl_2), λ_{max} (ϵ, $M^{-1}\ s^{-1}$): 354 (7300), 412 (7800), 510 (sh) nm. Anal. Calcd for **1** ($C_{32}H_{40}B_2NiS_4$): C, 60.70; H, 6.37; S, 20.25. Found: C, 60.49; H, 6.17; S, 19.85.

(10) Crystal data for **1**: $C_{32}H_{40}B_2NiS_4$; red block, monoclinic, $P2_1/n$, $a = 10.3144(9)$ Å, $b = 9.365(2)$ Å, $c = 16.7929(12)$ Å, $\beta = 107.624(9)°$, $V = 7242(3)$ Å^3, $Z = 2$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were not required because of the <10% variation in the integrated ψ-scan intensities. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The final residuals for 178 variables refined against 2006 unique reflections were $R(F) = 4.04\%$ and $R_w(F^2) = 8.53\%$.

(11) Halcrow, M. A.; Christou, G. *Chem. Rev.* **1994**, *94*, 2421−2481.

S0020-1669(96)00515-0 CCC: $12.00

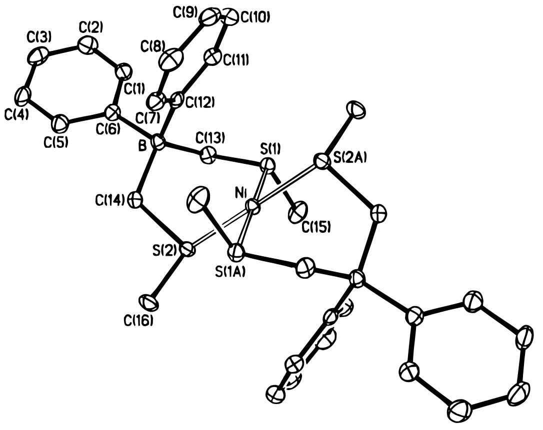

Figure 1. Thermal ellipsoid plot of **1** at the 35% probability level with hydrogen atoms removed for clarity. Selected bond distances (Å) and bond angles (deg): Ni−S(1), 2.244(1); Ni−S(2), 2.200(1); S(1)−Ni−S(1A), 180.0; S(2)−Ni−S(2A), 180.0; S(2)−Ni−S(1), 86.31(4); S(2)−Ni−S(1), 93.69(4).

has been noted in the structure of $[Ph_2B(pz)_2]_2Ni$, in which the Ph_{ax} centroid−Ni distance equals 3.45 Å.[12]

While the orientation of the Ph_{ax} groups suggests a measure of kinetic protection from exogenous substrates, the ^1H NMR spectrum at 27 °C reveals that in solution the Ph groups are magnetically equivalent. Cooling the solution to −50 °C results in a slow-exchange spectrum with two sets of Ph resonances.[13] These spectra are consistent with a fluxional process in which the twist-boat rings are inverting to a second twist-boat configuration, thus exchanging the Ph_{eq} and Ph_{ax} positions.

The cyclic voltammogram of **1** displayed a single, quasi-reversible wave at −421 mV (vs NHE)[14] assigned to the Ni(II/I) couple. This potential is intermediate between those of $[NiFe]H_2$ase and CODH and is significantly positive of that of Ni(tpttd), the only other NiS_4 chromophore that exhibits an electrochemically reversible Ni(II/I) couple ($E_{1/2} = -1180$ mV).[5] While thiolate ligation favors higher oxidation states (Ni(III)), thioethers stabilize lower oxidation states (Ni(I), Ni(0)). In general however, Ni(I) ions are unstable with respect to disproportionation to Ni(II) and Ni(0). For example, the more rigid square planar $[Ni([14]aneS_4)]^{2+}$ decomposes upon attempted reduction.[15] Remarkably, **1** may be chemically reduced with Na/Hg amalgam, resulting in a color change from red to yellow. Frozen THF solutions of the reduced species exhibited a rhombic EPR spectrum, Figure 2, with $g_1 = 2.27$, $g_2 = 2.11$, and $g_3 = 2.03$, consistent with metal-centered reduction.[16] The quasi-reversible reduction and the rhombic EPR signal are consistent with a Ni^IS_4 species which is structurally distinct from its square planar Ni(II) derivative.

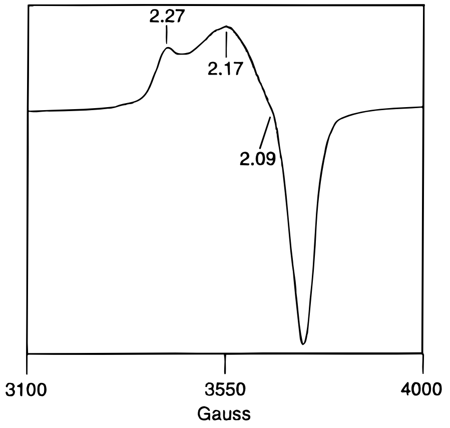

Figure 2. X-band EPR spectrum of $Na[(Ph_2Bt)_2Ni]$ in THF at 77 K.

The present system demonstrates that *thioethers* are competent ligands for modeling the Ni(II/I) potential for enzyme active sites that contain *thiolates* in the primary coordination sphere. We set forth several rationales that may explain this finding. First, if the cysteines are involved in H-bonding, their donor ability would be greatly diminished and the redox properties significantly altered.[6g,17] Under these conditions, thioethers may serve as more accurate ligand models in aprotic solvents. Second, the monoanionic borate chelates employed in this study allow the preparation of neutral complexes of divalent metal ions. The overall complex charge is a significant factor in determining redox potentials.[7] Finally, in the $[NiFe]H_2$ases and CODH the Ni ions are coupled to redox-active Fe centers.[1,2] The extent to which the Fe serves to modulate the Ni(II/I) potential, while not known, is certainly substantial.[18] Current efforts are directed toward the synthesis of $Ni-Fe_4S_4$ systems with the aim of evaluating the latter.

Acknowledgment. We gratefully acknowledge financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society (27076-G3), the NSF (OSR-9255223), the Exxon Educational Fund, and DuPont Central Research and Development. C.G.R. thanks the NSF for a National Young Investigator Award (1994−1999).

Supporting Information Available: Tables giving structure determination summary, atomic coordinates, bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters for **1** (5 pages). Ordering information is given on any current masthead page.

IC960515K

---

(12) Cotton, F. A.; Murillo, C. A. *Inorg. Chim. Acta* **1976**, *17*, 121−124.

(13) ^1H NMR (acetone-d_6, −50 °C): δ 7.54, 7.31, 7.17, 7.10, 7.00, 1.97, 1.84, 1.71, 1.59.

(14) $\Delta E = 150$ mV, $i_{pc}i_{pa}^{-1} = 0.9$. All experiments were recorded in a cell consisting of a glassy carbon working electrode (1 mm), a Pt wire counter electrode, and an Ag/AgCl reference electrode. CH_2Cl_2 solutions contained 0.1 M electrolyte ($[Bu_4N][PF_6]$) and 10 mM sample. Potentials were referenced to internal Fc/Fc^+ (+630 mV vs NHE, $\Delta E = 108$ mV, $i_{pc}i_{pa}^{-1} \approx 1.0$).

(15) Rosen, W.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4694−4697.

(16) **1** was stirred in THF over Na/Hg for 30 min. The solution was transferred to an EPR tube, and the spectrum was recorded at 77 K. An identical spectrum was obtained in DME.

(17) (a) Huang, J.; Ostrander, R. L.; Rheingold, A. L.; Leung, Y.; Walters, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6769−6776. (b) Krüger, H.-J.; Peng, G.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 734−742.

(18) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421−1423.