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Synthesis and Structure of a Water-Soluble Five-Coordinate Nickel Alkanethiolate Complex

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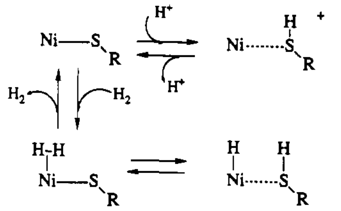
Research on the mechanism of hydrogenase (H_2-ase) enzymes has emphasized understanding the structure and function of the nickel site.[1] On the basis of EPR,[2] EXAFS,[3] XANES,[4] and ESEEM[5] studies, the nickel ion in H_2-ase appears to be mononuclear, redox active, and 5- or 6-coordinate with two to four S ligands and at least one N ligand. Hydrogenases catalyze H_2 activation/production and H_2/D^+ exchange.[1,6] Dihydrogen activation appears[7] to be heterolytic and to occur at the Ni site.[8] Most likely, this is assisted by a coordinated or nearby base[9] [Ni–B: + H_2 → Ni(σ-H_2)–B: → Ni(H)--BH; shown for B: = RS^- in (1)] and would require that there be either a vacant or labile site on the Ni ion.[13] It is possible that a Ni-bound thiolate could function as a base in H_2 cleavage [see (1)]. Given the acidity of some transition-metal σ-H_2 complexes,[10] this is not unreasonable. Ideally, the Ni–Se would be soluble in H_2O in order to mimic the biological conditions of the enzyme. However, the *thiolate chemistry of Ni(II) is dominated by a tendency to irreversibly form either clusters*[11] *or polymers,*[12] *especially in protic solvents.* This can be avoided by using aromatic thiolates[13–18] or rigid alkanethiolates,[19] thiocarboxylates,[20] or thioamidates.[21] Some of these have been shown to successfully model the inactive, aerobically isolated Ni(III) form of the H_2-ase.[19–21] Alkanethiolates are, of course, the preferred ligands since they would be expected to be more basic and more closely resemble a cysteinate residue. We report here the synthesis, structure, and solution properties of a water-soluble, 5-coordinate, mononuclear (alkanethiolato)nickel complex.



(1)

Complex **1**, $NiL_{S2(Me)N3(Pr)}$, was synthesized[22] using a Schiff base condensation at a Ni^{+2} ion template.[24] X-ray quality crystals were obtained by slowly cooling a MeOH solution to –25 °C.[25] The structure of **1** is illustrated in Figure 1. The geometry about the Ni(II) ion is nearly trigonal bipyramidal. The trigonal plane is composed of two alkanethiolates and an amine nitrogen, while the imine nitrogens assume axial positions. The most striking feature of this structure is that **1** is mononuclear despite the lack of bulky substituents near the alkanethiolate sulfurs. The only other known 5-coordinate complexes[13,14,16,17,26] incorporate aromatic thiolates and, in some cases, steric bulk to prevent oligomerization. Complex **1** is the first structurally characterized mononuclear, 5-coordinate alkanethiolate–nickel complex. The most reasonable explanation for the mononuclearity of **1** is that the rigidity of the imine linkages prevents expansion of the coordination sphere to accommodate a sixth, bridging sulfur, ligand. Also prominent in the crystal structure of **1** is the asymmetry in the Ni–S distances; Ni–S(2) is substantially longer

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(22) Under anaerobic conditions at 0 °C, $Ni(OAc)_2 \cdot 4H_2O$ (0.747 g, 3 mmol) was combined with 2,5-dihydroxy-2,5-dimethyl-1,4 dithiane[23] (0.541 g, 3 mmol), NaOH (0.24 g, 6 mmol), and 3,3′-iminobis(propylamine) (0.42 mL, 3 mmol) in MeOH and stirred overnight. Slow cooling afforded 0.25 g (25%) of dark green X-ray quality crystals of **1**. Anal. Calcd for $C_{12}H_{23}N_3S_2Ni$: C, 43.39; H, 6.98; N, 12.65; S, 19.30. Found: C, 43.46; H, 7.17; N, 12.43; S, 18.62. μ_{eff}(MeOH) = 2.97 μ_B; μ_{eff}(solid state) = 2.86 μ_B.

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(25) Crystallographic data [Mo Kα (λ = 0.710 69 Å) radiation, Syntex $P2_1$ diffractometer, 130 K] for **1** are as follows: $C_{12}H_{23}N_3S_2Ni$, monoclinic, space group $P2_1/n$, $a = 8.374(4)$ Å, $b = 15.383(5)$ Å, observed reflections $c = 11.806(5)$ Å, $\beta = 107.57(3)°$, $V = 1449.9(10)$ Å^3, $Z = 4$, 1449 observed reflections ($F > 4.0\sigma(F)$), $R = 0.0366$, $R_w = 0.0290$. The structure was solved by direct methods (SHELXTL PLUS, version 4.2, 1990).

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(27) Shown in a packing diagram of the supplementary material: S(2) is within van der Waals contact of three hydrogens [S(2)···H(3c) = 2.87 Å, S(2)···H(2a) = 3.02 Å, S(2)···H(6a) = 2.87 Å] on two adjacent molecules that are related by a crystallographic inversion center.

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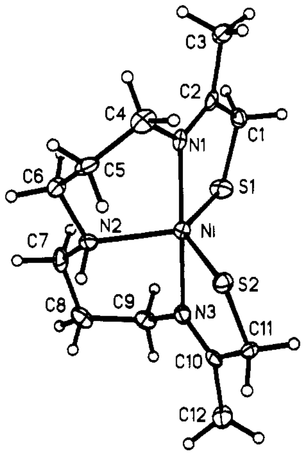

Figure 1. ORTEP diagram of $NiL_{S2(Me)N3(Pr)}$ (**1**). Selected distances (Å) and angles (deg): Ni–S(1), 2.306(2); Ni–S(2), 2.359(2); Ni–N(1), 2.065(4); Ni–N(2), 2.068(4); Ni–N(3), 2.048(4); S(1)–Ni–S(2), 135.3(1); S(1)–Ni–N(1), 84.7(1); S(2)–Ni–N(1), 99.1(1); S(2)–Ni–N(2), 101.0(1); S(2)–Ni–N(3), 83.6(1); N(1)–Ni–N(2), 92.7(1); N(1)–Ni–N(3), 177.3(2).

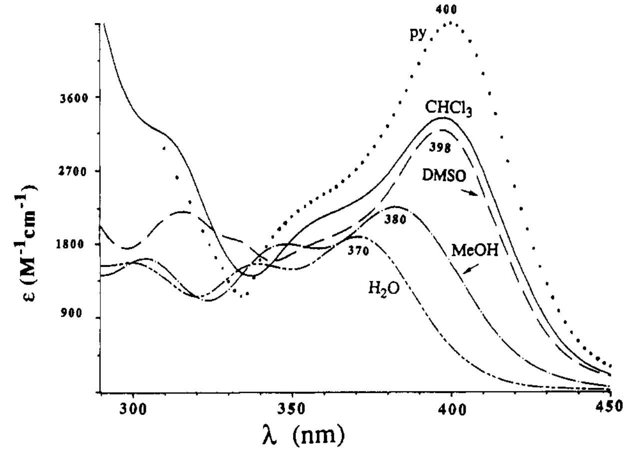

Figure 2. Electronic spectra of **1** in aprotic (py (···), $CHCl_3$ (—), DMSO (– –)) vs protic (MeOH (—), H_2O (– - - -)) solvents. Protic solvents cause the charge-transfer band at 398–400 nm to blue-shift (26–30 nm), presumably by hydrogen-bonding to the thiolate sulfurs.

than Ni–S(1) [2.359(2) Å vs 2.306(2) Å]. Intermolecular S(2)···H interactions[27] are probably responsible for the long Ni–S(2) distance. S···H bonding has been observed in the solid state in at least two other nickel structures.[21,28]

Evidence for S···H interaction is more clearly seen in the solution electronic spectra of **1** (Figure 2). Complex **1** is soluble in a wide variety of solvents, but it is particularly soluble in protic solvents, especially in H_2O. Other examples of water-soluble Ni thiolates have been reported;[28] however, none of these possess the more biologically-relevant 5- or 6-coordinate geometry. The spectra shown in Figure 2 contain charge-transfer bands in the range 300–450 nm. In all of the aprotic solvents investigated,[29] the lowest energy band occurs at approximately the same energy. In protic solvents, however, this band blue-shifts (26–30 nm) in proportion to the proton-donor ability of the solvent. If one assumes that these bands are sulfur-to-nickel charge-transfer bands,[30] then these observations suggest that intermolecular S···H bonding[31] between **1** and solvent is stabilizing the π-symmetry sulfur orbitals relative to the metal d orbitals. The observed blue shift (30 nm or 5.8 kcal/mol) in going from $CHCl_3$ to H_2O is remarkably close to the energy of an H-bond (2–10 kcal/mol).[32] Similar blue shifts have been observed with water-solubilized, synthetic Fe_4S_4 clusters.[33] Solvent binding, and/or decoordination of an amine[31] or thiolate, can be ruled out as being responsible for the observed spectral differences of **1** in protic vs aprotic solvents, since the lower energy d–d transitions (600–1000 nm; not shown)[29] do not shift or decrease in intensity. Demetalation can also be ruled out by the fact that no free ligand is observed in the ^1H NMR spectra in either D_2O or CD_3OD.[34]

The rigidity of the ligand in **1** affects both the ligand-binding characteristics and the redox behavior. Strongly binding solvents (py, Me-Im, MeCN) and anionic ligands (CN^-, N_3^-) do not appear to bind to the Ni ion of **1**, on the basis of electronic spectral studies. And, although solutions of **1** react with oxidizing agents [I_2, $Fe(CN)_6^{3-}$] to give weak transient EPR signals,[35] **1** does not appear to react with common reducing agents (e.g., $S_2O_4^{2-}$, BH_4^-). This contrasts with previously reported 5-coordinate $Ni^{II}S_2N_3$ compounds,[16,17] which form reduced Ni(I) derivatives upon addition of $S_2O_4^{2-}$, or BH_4^-.

In summary, both the solid-state and solution properties indicate that the nickel-bound alkanethiolate sulfurs of **1** have an affinity for protons, suggesting that it is possible, in the metalloenzyme hydrogenase, that sulfur can act as either a proton storage site, or as a participant in the promotion of heterolytic H_2 cleavage. The observed S···H(H_2O) interaction (~5.8 kcal/mol) with **1** is, of course, small relative to an S–H (87 kcal/mol) bond. The rigidity of the Schiff-base ligand of **1** favors a mononuclear structure and inhibits reduction to Ni(I) and the binding of additional ligands.

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Supplementary Material Available: A packing diagram for **1** showing S···H interactions (Figure S-1), a textual presentation of the crystallographic details, and tables giving data collection parameters, atomic positional and isotropic thermal parameters, anisotropic thermal parameters, bond distances and angles, and hydrogen atom positional and isotropic thermal parameters for **1** (11 pages). Ordering information is given on any current masthead page.

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(29) Electronic spectral data (nm (ε)) for $NiL_{S2(Me)N3(Pr)}$ are as follows. H_2O: 296 (1600), 340 (1500), 370 (1900), 614 (200), 960 (30). MeOH: 304 (1600), 346 (1800), 380 (2300), 624 (204), 970 (50). DMF: 312 (2015), 398 (3070), 642 (160), 964 (22). MeCN: 310 (2290), 396 (2570), 638 (160), 902 (40). Py: 400 (4500), 644 (190), 968 (24). $CHCl_3$: 398 (3300), 626 (170), 976 (18). MeIm: 396 (3500), 640 (210), 974 (30). This is best illustrated by comparing the d–d transitions in $CHCl_3$ vs MeOH.

(30) The only alternative assignments for a band in this region, with the measured extinction coefficient, would be as a nickel-to-imine π* or imine π-to-π* charge-transfer band. However, in order for the imine nitrogens to H-bond without de-coordinating, N═C hydrolysis would have to occur, which would induce decomposition (to thioacetate + free amine).

(31) N···H bonding can be ruled out because this would require decoordination or hydrolysis.

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(34) ^1H NMR data for $NiL_{S2(Me)N3(Pr)}$ are as follows. In D_2O: δ 341, 277, 264, 160, 127, 124, 110, 83.5, 54.5, 45.6, 32.0, 2.91, –2.58, 0.47, –6.07, –13.0, –15.9. In CD_3OD: δ 315, 261, 257, 158, 140, 121, 106, 85.8, 79.6, 59.8, 50.8, 28.8, 1.01, –3.68, -0.67, –5.96, –13.2, –14.7.

(35) $g = 2.035, 2.007$ in Me-Im at 10 K.