In summary, we have established the importance of geometry optimization with electron correlation in the 1,2-hydrogen shift in H_2O_2 and in the gas-phase oxygen transfer from hydrogen peroxide to ammonia. The "electrophilic" oxygen atom has a full octet of electrons around oxygen in the transition state, and the leaving group is essentially neutral water.

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Registry No. H_2O_2, 7722-84-1; NH_3, 7664-41-7.

X-ray Absorption Spectroscopic Structural Investigations of the Ni Site in Reduced *Thiocapsa roseopersicina* Hydrogenase

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Hydrogenases (H_2ases) are key enzymes in anaerobic metabolism that catalyze the reversible oxidation of H_2.[1,2] Hydrogenases may be divided into three classes based on the composition of their inorganic cofactors. These classes are the Fe-only, Fe–Ni, and Fe–Ni–Se enzymes.[3] The latter two classes of enzymes contain unusual redox-active Ni centers. EPR has been extensively employed to monitor the redox chemistry of the Ni site and reveals that oxidized (as isolated) enzymes display characteristic signals that have been assigned to tetragonal, *formally* Ni(III) complexes (forms A and B).[4] Upon reduction, these signals disappear, and the signal arising from a two-electron-reduction product (form C) appears.[4] Electron spin echo envelope modulation studies (ESEEM) have been performed on H_2ases from *Thiocapsa roseopersicina*,[5] *Methanobacterium thermoautotrophicum*,[6] and *Desulfovibrio gigas*[7] and indicate the presence of one N atom near the Ni center in *T. roseopersicina* and *M. thermoautotrophicum* F_{420}-reducing H_2ase and in the *D. gigas* enzyme, but not in the *M. thermoautotrophicum* viologen-reducing enzyme. X-ray absorption spectra obtained on H_2ases from chemotrophs have been interpreted in terms of largely S-donor environments,[8] involving at least three and as many as six S-donor ligands. The lack of structure near the Ni K-edge in the *D. gigas* enzyme is consistent with either a 5- or 6-coordinate environment.[9] These results contrast with recent EPR investigations employing ^{33}S-labeled H_2ase from *Wolinella succinogenes* that are consistent with only one or two S-donor ligands in the first coordination sphere of Ni.[10] We report here the analysis of XAS data obtained from the Fe–Ni H_2ase from the purple photosynthetic bacterium, *T. roseopersicina*, poised in form C. These results provide the first information about the Ni-site structure of this key form of the enzyme and the first direct evidence for a mixed-ligand Ni environment in this class of H_2ase.

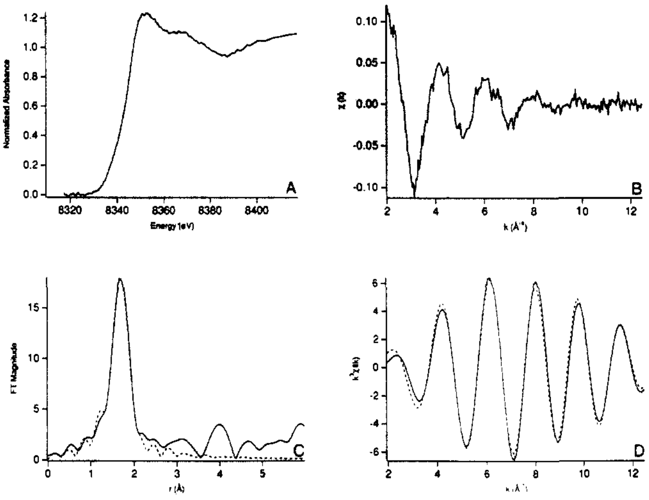

Figure 1. X-ray absorption spectra for the Ni center in *T. roseopersicina* hydrogenase (form C) (solid lines) and fits (dashed lines). Details of the fits are given in Table I. (A) The normalized Ni K-edge spectrum. (B) The unfiltered, base-line-corrected raw EXAFS spectrum. (C) Fourier transform of the EXAFS data over the *k* range 2–12.5 and the Fourier transform of the first coordination shell fit. (D) First coordination shell Fourier-filtered EXAFS and fit.

T. roseopersicina was cultured and the H_2ase isolated and assayed as previously described,[11] employing preparative electrophoresis in the final purification step. The enzyme was fully reduced by H_2 and then oxidized to form C by the addition of benzylviologen, using EPR spectroscopy to monitor the redox state of the Ni center. The sample used in the XAS studies was prepared in 20 mM Tris·HCl (pH 8) buffer containing 20% glycerol prior to concentration to ca. 0.3 mM Ni. The sample was analyzed for Fe and Ni content by graphite furnace atomic absorption spectroscopy following data collection and found to have an Fe:Ni ratio ((7 ± 1):1) consistent with published values.[12] X-ray fluorescence data was collected by using a 13-element Ge array detector from frozen solutions held at 77 K in a cryostat on beam line X9A at the National Synchrotron Light Source (2.53 GeV, ca. 110–180 mA) employing a monochromator with Si[111] crystals (resolution ca. 1 eV). Spectra were calibrated to the first inflection in a Ni foil spectrum. Transmission data from model compounds ($[Ni(Im)_6](BF_4)_2$[13] and $(Et_4N)_2[Ni(p\text{-}SC_6H_4Cl)_4]$[14]) that were diluted with boron nitride to reduce thickness effects were collected at ambient temperature and employed in analyzing the protein data over the *k* range 2–12.5 using the amplitude and phase functions of McKale et al. that were calculated by using

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Table I. Least-Squares Refinements of Fourier-Filtered EXAFS Data[a]

back-transform window	no. of scattering atoms	r,[b] Å	$\Delta\sigma^2 \times 10^3$,[c] Å^2	correlation coefficients > 0.6	R[d]
r = 1.1–2.3 Å	5	Ni–S = 2.214 (3)	3.0 (4)		1.51
	4 1	Ni–S = 2.226 (3) Ni–N = 2.055 (2)	5.1 (4) −11.7		0.67
	3 2	Ni–S = 2.200 (2) Ni–N = 2.057 (2)	4.2 (3) −8.6 (2)	$r_S/r_N = -0.64$	0.44
	2 **3**	**Ni–S = 2.215 (3)** **Ni–N = 2.0.53 (3)**	**1.0** **−4.5 (2)**	$\boldsymbol{r_S/r_N = -0.77;\ \sigma_S/\sigma_N = -0.67}$	**0.40**
	1 4	Ni–S = 2.222 (4) Ni–N = 2.044 (2)	−3.3 (3) −4.5 (2)	$r_S/r_N = -0.69;\ r_S/\sigma_N = -0.71;\ r_N/\sigma_S = 0.74$	0.44
	5	Ni–N = 2.058 (2)	−5.9 (2)		1.08

[a] The fit shown in boldface type is the one displayed in Figure 1. The use of unfiltered data does not lead to substantial changes in bond lengths or other adjusted parameters. [b] Bond lengths for first coordination sphere atoms in compounds of known structure are generally reproduced within 0.02 Å. [c] $\Delta\sigma^2 = \sigma^2$ (fit) − σ^2 (model). [d] $R = [\sum k^6(\chi_c - \chi)^2/n]^{1/2}$.

a full curved wave formalism[15] and following a published fitting strategy.[16]

The Ni K-edge absorption spectrum obtained from *T. roseopersicina* H_2ase form C is shown in Figure 1. The edge is distinct from those published from H_2ase from *D. gigas* and is indicative of the presence of more O,N-donor ligands.[17] The edge does not reveal any evidence of a 1s → 4p$_z$ transition (with shakedown contributions) that is observed in square-planar complexes,[9] nor is a strong 1s → 3d transition characteristic of tetrahedral geometry observed.[9] This result indicates either a 5- or 6-coordinate Ni geometry.

In contrast to previous fits of Fe–Ni H_2ases, analyses of the first coordination sphere data from *T. roseopersicina* are consistent only with a mixed-donor coordination environment and cannot be fit by either exclusively S(Cl) donors or N,O donors (Table I, Figure 1). The best fits were obtained for a coordination number of 5, with 2 ± 1 S(Cl)-donor ligands at a distance of 2.22 (2) Å and 3 ± 1 N,O-donor ligands at an average distance of 2.05 (2) Å (Table I). The Ni K-edge spectrum from *T. roseopersicina* H_2ase (form C) and the results from the analysis of the first coordination sphere Ni EXAFS data bear a striking resemblance to those recently published for the oxidized (as isolated) form of an Fe-Ni-Se enzyme (3–4 O,N donors at 2.06 Å, 1–2 S(Cl) donors at 2.17 Å, and 1 Se at 2.44 Å)[18] and suggest that such mixed-donor environments are typical of both classes of Ni-containing H_2ases. There is no evidence to support the existence of a long (ca. 2.4 Å) Ni–S bond in the Fe–Ni enzyme. The Ni–S distance found is considerably shorter than those exhibited by 6-coordinate Ni(II) thiolate complexes (ca. 2.4–2.5 Å)[19–21] and the only structurally characterized Ni(III) complex with S-donor ligands (ca. 2.3 Å).[20] These results appear to rule out a 6-coordinate Ni center *in form C*. The potential presence of a hydride or dihydrogen ligand in form C[22] would be expected to contribute to the edge structure, but not to the EXAFS spectrum.[17] Thus, the results do not rule out a 5-coordinate complex composed of four endogenous ligands and a hydride.

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New Structural Class of Solid-State Oxide

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We recently described the relevance of the optical properties of the new borate $Sr_3Sc(BO_3)_3$ doped with the ion Cr^{3+} to the development of new laser materials.[1] We have now found that this material is only one example of a large and versatile family of solid-state oxides. This family of oxides currently comprises the borates of formula $A_6MM'(BO_3)_6$ where A = Sr or Ba; M = lanthanide, Y, Sc, In, Bi, Ca, Mg, or Cd; and M′ = small lanthanide, Y, Sc, Cr, Mn, Fe, Co, Ni, Zr, Sn, Ru, Rh, Hf, Al, Ga, In, or Mg. We have prepared more than 125 members of the family; representative formulas and their lattice parameters are listed in Table I.[2] All derivatives are readily prepared by standard high-temperature techniques with annealing temperatures ranging from 1175 to 1375 K.

The structure adopted by these materials is best appreciated by inspection of drawings **1** and **2**. Atoms M and M′ occupy octahedral sites that are bridged by triangular BO_3 groups to form a one-dimensional chain, **1**. These chains pack in a trigonal

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(2) Each cell parameter was determined by least-squares analysis of 11 reflections obtained with an automated Philips powder diffractometer and corrected by using NBS Si standard 640b.

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