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	Ni–S = 2.226 (3)	5.1 (4)		0.67
	1	Ni–N = 2.055 (2)	−11.7		
	3	Ni–S = 2.200 (2)	4.2 (3)	$r_S/r_N = -0.64$	0.44
	2	Ni–N = 2.057 (2)	−8.6 (2)		
	2	**Ni–S = 2.215 (3)**	**1.0**	$r_S/r_N = -0.77$; $\sigma_S/\sigma_N = -0.67$	**0.40**
	3	**Ni–N = 2.0.53 (3)**	**−4.5 (2)**		
	1	Ni–S = 2.222 (4)	−3.3 (3)	$r_S/r_N = -0.69$; $r_S/\sigma_N = -0.71$; $r_N/\sigma_S = 0.74$	0.44
	4	Ni–N = 2.044 (2)	−4.5 (2)		
	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] $\Delta\sigma^2 = \sigma^2\,(\mathrm{fit}) - \sigma^2\,(\mathrm{model})$. [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.

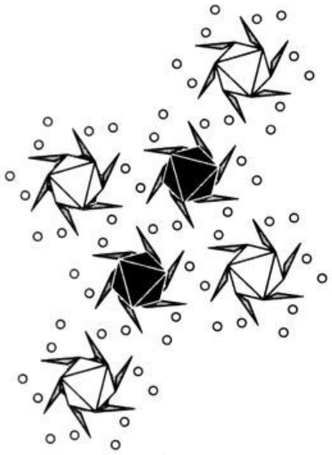
Table I. Cell Parameters for Selected Members of the Family $A_6MM'(BO_3)_6$

	a, Å	c, Å	V, Å³
$Sr_3Sc(BO_3)_3$[a]	12.135 (1)	9.184 (1)	1171.3 (3)
$Sr_3Ho(BO_3)_3$	12.509 (1)	9.254 (1)	1254.0 (2)
$Sr_6HoSc(BO_3)_6$[a]	12.285 (3)	9.268 (2)	1211.2 (5)
$Sr_6YAl(BO_3)_6$	12.190 (2)	9.109 (5)	1172.3 (1)
$Ba_6YFe(BO_3)_6$	12.797 (1)	9.372 (2)	1329.1 (2)
$Sr_6CaZr(BO_3)_6$	12.453 (1)	9.367 (1)	1258.0 (5)
$LaSr_5YMg(BO_3)_6$	12.237 (2)	9.215 (3)	1194.9 (4)
$LaSr_2Mg(BO_3)_3$	12.318 (1)	9.254 (2)	1216.1 (2)

[a] Single-crystal data.

manner according to view **2** along the chain axis; the Sr atoms (small open circles) bridge adjacent chains by occupation of 9-coordinate sites. In each chain the octahedral sites of M and M′ are crystallographically and chemically distinct. The site M is larger and exhibits an elongation along the chain axis whereas site M′ is smaller and compressed along the same axis. This dissimilar nature of the octahedra contributes to the existence of the large number of ordered materials within the family.

1



2

The largest subgroup of the structural type forms with M and M′ as tripositive cations in conjunction with the A atom Sr. The formula with M = M′ = Sc corresponds to the material $Sr_3Sc(BO)_3$, and the formula with M = Ho and M′ = Sc corresponds to the material $Sr_6HoSc(BO_3)_6$. The ordering that occurs between the two different octahedral sites when occupied by atoms M and M′ of disparate sizes is one of the critical issues concerning the crystal chemistry of this family. A structure determination of the derivative $Sr_6HoSc(BO_3)_6$ indicates that it crystallizes in a selective manner with the Ho atom preferring the larger octahedral site and the Sc atom the smaller site.[3] The Ho–O and Sc–O distances, 2.296 (4) and 2.092 (4) Å, respectively, are consistent with values computed from crystal radii.[4] The crystal used for the structure determination was grown by melting the stoichiometric compound at 1773 K in a Pt crucible followed by cooling at 4 K/h to 1273 K and 40 K/h to 298 K. A small, light pink crystal was cleaved from the resulting transparent button and mounted for X-ray analysis.

We have found that Ba analogues crystallize in this structure type only in those instances where atoms M and M′ have dissimilar sizes; derivatives with atoms M and M′ of similar sizes form a different, unique family of layered materials.[5] For example, the compound $Ba_6TbSc(BO_3)_6$ crystallizes in the chain structure whereas the compound $Ba_6HoSc(BO_3)_6$ crystallizes in the layered structure.

The total formal charge (+6) of atoms M and M′ may be realized by the combination of charges 2 + 4 as exemplified by the compounds $Sr_6CaZr(BO_3)_6$ and $Sr_6CdSn(BO_3)_6$. Smaller dipositive cations may be incorporated in compounds of the type $LaSr_5YMg(BO_3)_6$ and $LaSr_2Mg(BO_3)_3$ where the La atom likely occupies a 9-coordinate site. In this way, a variety of derivatives containing, for example, dipositive transition-metal ions may be accessed. From consideration of current results it appears likely that all cations of formal charge +2, +3, or +4 that prefer octahedral or 9-coordinate environments can be incorporated into this structural type in significant amounts.

A full account of the crystal chemistry of these families of materials[5] as well as results on the optical and magnetic properties of selected members will be given in future articles.

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Supplementary Material Available: Listing of 115 derivatives with cell parameters and crystallographic data for the compound $Sr_6HoSc(BO_3)_6$ (8 pages); listing of observed and calculated structure factors for $Sr_6HoSc(BO_3)_6$ (5 pages). Ordering information is given on any current masthead page.

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(3) Crystal and refinement data: space group $R\bar{3}$, $a = 12.285$ (3) Å, $c = 9.268$ (2) Å, $V = 1211.2$ (5) Å³, $Z = 6$; 693 observations with $I > 3\sigma(I)$ and 50 variables; $R = 0.027$, $R_w = 0.041$. A constrained refinement indicates a disorder of 8% between the Ho and Sc sites. Single-crystal X-ray diffraction data were collected on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation to $\sin \theta_{max}/\lambda = 1.22$ Å^{-1}.

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Quantifying Acid–Base Properties of Organic Functional Groups at a Polyethylene–Water Interface by Photoacoustic Calorimetry

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This paper describes the use of photoacoustic calorimetry (PAC)[1] to characterize acid–base equilibria involving organic chromophores covalently attached at the interphase between surface-functionalized polyethylene (PE) film[2,3] and water. We use proton transfer reactions to define the polarity and solvating capability of the interphase between organic surfaces and water.[4] Characterizing these physical–organic properties of interphases is difficult: light scattering at interfaces (especially *rough* interfaces) complicates many UV–vis absorption and fluorescence methods; infrared spectroscopy cannot be applied routinely to systems involving water; thermometric and conductometric methods are insensitive for solids having low surface areas. The measurement of the contact angle of buffered water on surfaces as a function of pH—"contact angle titration"—yields valuable information about acid–base equilibria,[3] but depends on unverified assumptions.[5]

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