pyramidal geometry for the anion in the ion pair and a monodentate, axial interaction between the cation and anion, although the C_{2v} and C_{4v} structures cannot be ruled out. The synthesis of the mixed chlorine/fluorine species was also carried out, for all combinations of Cl and F. However, all attempts to synthesize the $SiCl_5^-$ ion were unsuccessful, presumably due to the size of the chloride ligand. The results also indicate that five-coordinate silicon anions are quite stable entities and may well be the active intermediates in those organosilicon reactions where the fluoride anion F^- is used as a catalyst.

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Registry No. $Cs^+SiF_5^-$, 71661-67-1; $Cs^+SiClF_4^-$, 71697-69-3; $Cs^+SiCl_2F_3^-$, 71661-68-2; $Cs^+SiCl_3F_2^-$, 71661-69-3; $Cs^+SiCl_4F^-$, 71697-70-6; SiF_4, 7783-61-1; $SiCl_4$, 10026-04-7; $SiClF_3$, 14049-36-6; $SiCl_2F_2$, 18356-71-3; $SiCl_3F$, 14965-52-7; CsF, 13400-13-0; KF, 7789-23-3; CsCl, 7647-17-8.

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Group 3A and 4A Substituted AB$_5$ Hydrides

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Crystallographic cell volume data are presented for a series of alloys $LaNi_{5-x}M_x$ (M = Al, Ga, In, Si, Ge, Sn) for x = 0–0.5. Pressure–composition desorption isotherms were measured for the hydrides of $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ at 30, 40, and 60 °C. From plots of ln P vs. $1/T$ the enthalpies and entropies of transition were calculated to be −8.5 kcal/mol of H_2 and −27.3 cal/(mol of H_2 deg) for $LaNi_{4.6}Si_{0.4}H_y$ and −8.2 kcal/mol of H_2 and −26.5 cal/(mol of H_2 deg) for $LaNi_{4.6}Ge_{0.4}H_y$. The thermodynamic quantities as well as the hysteresis behavior of these hydrides are compared to data previously obtained for the hydrides of $LaNi_{4.6}Al_{0.4}$, $LaNi_{4.6}Ga_{0.4}$, $LaNi_{4.6}In_{0.4}$, and $LaNi_{4.6}Sn_{0.4}$.

Alloys with the $CaCu_5$ structure have been extensively studied because of their ability to absorb and desorb large quantities of hydrogen gas rapidly.[1b] It has recently been observed that relatively small mole fractions of a third element, for example Al, when substituted for Ni, can have a large effect on the hydrogen dissociation pressure of the corresponding hydride.[2-5] Decomposition isotherms for the series of alloy hydrides $LaNi_{4.6}M_{0.4}H_y$ (M = Al, Ga, In, Sn) have been published elsewhere.[6,7] We now wish to report cell volume data for the alloy series $LaNi_{5-x}Ga_x$ (x = 0–0.5), $LaNi_{5-x}In_x$ (x = 0–0.5), $LaNi_{5-x}Si_x$ (x = 0–0.5), $LaNi_{5-x}Ge_x$ (x = 0–0.5), and $LaNi_{5-x}Sn_x$ (x = 0–0.5) and pressure–composition isotherms for the hydrides $LaNi_{4.6}Si_{0.4}H_y$ and $LaNi_{4.6}Ge_{0.4}H_y$.

Experimental Section

Alloys were prepared by using standard arc-melting techniques under an atmosphere of argon. Alloy lattice parameters were determined from X-ray powder diffraction photographs using filtered Fe Kα radiation. A least-squares computer program was used to obtain the final lattice parameters. The procedure for measuring pressure–composition desorption isotherms of the hydrides was identical with that described previously.[2]

Results and Discussion

Plots of the crystallographic unit cell volume, v, vs. the mole fraction x, of the group 3A and 4A element substituents are given in Figure 1a for all six ternary alloys. A more detailed crystallographic analysis will be published elsewhere.[8] Desorption isotherms for the hydrides $LaNi_{4.6}Si_{0.4}H_y$ and $LaNi_{4.6}Ge_{0.4}H_y$ are shown in Figure 2 for temperatures of 30 and 60 °C. Isotherms were also obtained at 40 °C but are not shown. Table I lists thermodynamic data obtained for the hydrides $LaNi_{4.6}M_{0.4}H_y$ (M = Al, Ga, In, Si, Ge, Sn) from plots of log P_{plateau} vs. $1/T$. The pressures used in the van't Hoff plots were taken near the middle of the two-phase plateau

Table I. Thermodynamic and Cell Volume Data for 3A and 4A Substituted $LaNi_5$ Alloys

alloy	$\Delta H_{\alpha\to\beta}$, kcal/mol of H_2	$\Delta S_{\alpha\to\beta}$, cal/(deg mol of H_2)	ΔG,[b] kcal/mol	cell vol, Å^3
$LaNi_{4.6}Al_{0.4}$	−8.7	−26.1	−1.05	87.9
$LaNi_{4.6}Ga_{0.4}$	−8.4[a]		−0.7	88.1
$LaNi_{4.6}In_{0.4}$	−9.5	−26.5	−1.7	91.0
$LaNi_{4.6}Si_{0.4}$	−8.5	−27.3	−0.5	86.9
$LaNi_{4.6}Ge_{0.4}$	−8.2	−26.5	−0.4	87.8
$LaNi_{4.6}Sn_{0.4}$	−9.2	−26.2	−1.5	91.0

[a] Calculated from a single desorption isotherm assuming a value of −26.3 for $\Delta S_{\alpha\to\beta}$. [b] Calculated for 20 °C.

Table II

alloy	temp, °C	H atoms/ mol of alloy[a] (β phase)
$LaNi_{4.6}Al_{0.4}$	30	4.7
$LaNi_{4.6}Ga_{0.4}$	22	4.5
$LaNi_{4.6}In_{0.4}$	30	4.6
$LaNi_{4.6}Si_{0.4}$	30	3.5
$LaNi_{4.6}Ge_{0.4}$	30	4.0
$LaNi_{4.6}Sn_{0.4}$	30	4.2

[a] Values obtained by a visual estimate of the two-phase plateau region and β-phase boundary.

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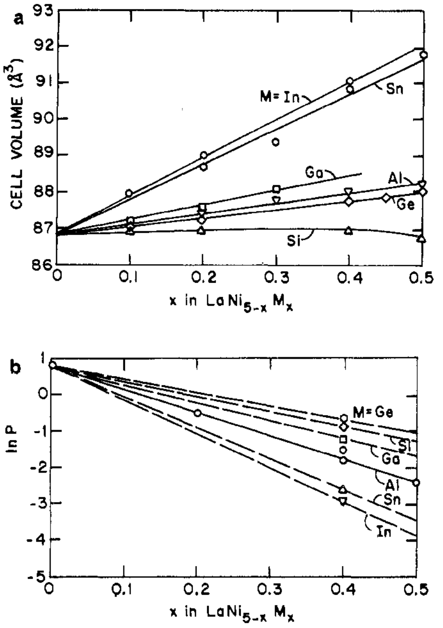

Figure 1. (a) Crystallographic cell volume vs. alloy composition ($\mathrm{LaNi_{5-x}M_x}$). (b) Hydrogen plateau pressure at 20 °C vs. alloy composition ($\mathrm{LaNi_{5-x}M_x}$).

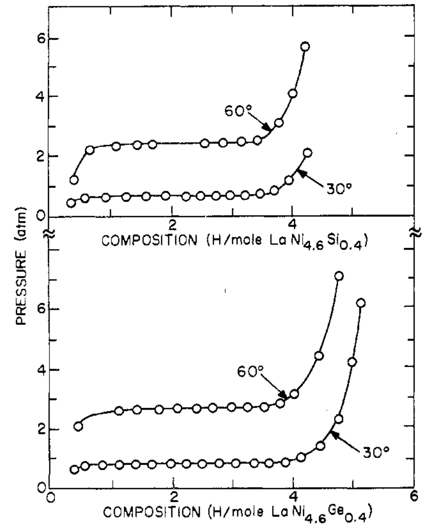

Figure 2. Desorption isotherms at 30 and 60 °C for the hydrides $\mathrm{LaNi_{4.6}Si_{0.4}H_y}$ and $\mathrm{LaNi_{4.6}Ge_{0.4}H_y}$.

region. Table II gives the approximate composition of the hydride phase near room temperature (22–30 °C) obtained by a visual estimation of the boundary between the two-phase plateau region and the single-phase hydride region of the appropriate pressure–composition isotherm.

Table II shows that the limiting β-phase compositions are relatively constant for group 3A substitutions with $x = 0.4$. However, the group 4A elements show a roughly 10–25% reduction in hydride composition over the 3A elements and an approximately 20% increase in hydrogen capacity on going down the periodic table from Si to Sn. It is to be noted that the β-phase composition for $\mathrm{LaNi_5}$ hydride is ~6.0.

The trend in crystallographic cell volumes for the alloys shown in Figure 1a (Si < Ge < Al < Ga < Sn < In) is consistent with the known variations in metallic radii of these elements.[9] Although Wells does not give a value for the metallic radius of silicon, the interatomic distance for Si is smaller than for Ge in diamond-type structures.[9]

A comparison of the cell volumes of the alloys in Table I with the free energies of formation of the corresponding hydrides confirms, in general, the previously observed, approximately linear correlation of decreasing free energy of formation of $\mathrm{AB_5}$ hydrides with increasing cell volume.[3,10] However, detailed examination of the data reveals a reversal of the trend for the two hydride pairs $\mathrm{LaNi_{4.6}Al_{0.4}H_y}$–$\mathrm{LaNi_{4.6}Ga_{0.4}H_y}$ and $\mathrm{LaNi_{4.6}Si_{0.4}H_y}$–$\mathrm{LaNi_{4.6}Ge_{0.4}H_y}$. For both pairs, there occurs a change in the electronic structure of the substituted element from empty 3d orbitals to filled 3d orbitals. Thus, the observed reversal in hydride free energies may indicate the involvement of specific metal–hydrogen bonding properties in addition to the previously noted importance of metal–hydrogen[11] and hydrogen–hydrogen[12] distances on the dissociation pressure of the alloy hydrides.

Table III

alloy	temp, °C	H/ mol of alloy	P_{Abs}, atm	P_{Des}, atm	P_A/P_D
$\mathrm{LaNi_{4.6}Al_{0.4}}^{a}$	30	3.09	0.31	0.28	1.11
$\mathrm{LaNi_{4.6}Al_{0.4}}^{a}$	48	3.10	0.71	0.64	1.11
$\mathrm{LaNi_{4.6}Al_{0.4}}^{a}$	60	3.10	1.16	1.00	1.16
$\mathrm{LaNi_{4.6}Al_{0.4}}^{a}$	80	2.84	2.41	2.05	1.18
$\mathrm{LaNi_{4.6}Al_{0.4}}^{a}$	100	2.75	4.77	4.20	1.14
$\mathrm{LaNi_{4.6}In_{0.4}}$	30	1.96	0.097	0.095	1.02
$\mathrm{LaNi_{4.6}Si_{0.4}}$	30	1.58	0.73	0.67	1.09
$\mathrm{LaNi_{4.6}Si_{0.4}}$	40	1.23	1.11	1.04	1.07
$\mathrm{LaNi_{4.6}Ge_{0.4}}$	30	1.32	0.85	0.78	1.09
$\mathrm{LaNi_{4.6}Ge_{0.4}}$	40	1.97	1.31	1.21	1.08
$\mathrm{LaNi_{4.6}Sn_{0.4}}^{b}$	20	2.41	0.078	0.079	0.99
$\mathrm{La_{1.05}Ni_{4.6}Sn_{0.4}}^{b}$	32	2.38	0.162	0.156	1.04
$\mathrm{LaNi_5}^{c}$	20	3.0	2.0	1.6	1.25

[a] From ref 3. [b] Two different samples. [c] From ref 14.

An approximately linear correlation had been found between the equilibrium hydrogen pressure near 20 °C and the amount of aluminum substitution.[3] In Figure 1b, similar plots of ln P vs. x in $\mathrm{LaNi_{5-x}M_x}$ are shown, based on the assumption that the other group 3A and 4A element substitutions follow the same linear relationship as found in the case of aluminum.

In general, absorption pressures do not appear to be as reproducible as desorption pressures and no extensive data for the absorption isotherms were obtained. However, for practical applications of metal hydrides, absorption pressures need to be known at least approximately. Therefore, single data points on the absorption pressure–composition diagram were taken at several temperatures for the alloys listed in Table III. The reason for the reduction in hysteresis upon substitution of a 3A or 4A element for nickel compared to $\mathrm{LaNi_5}$ is not clear but is an important benefit in some proposed practical applications of metal hydrides.[13]

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Registry No. $\mathrm{LaNi_5}$, 62651-39-2; $\mathrm{LaNi_{4.6}Al_{0.4}}$, 71565-55-4; $\mathrm{LaNi_{4.6}Ga_{0.4}}$, 71565-56-5; $\mathrm{LaNi_{4.6}In_{0.4}}$, 69179-14-2; $\mathrm{LaNi_{4.6}Si_{0.4}}$, 71565-57-6; $\mathrm{LaNi_{4.6}Ge_{0.4}}$, 71565-58-7; $\mathrm{LaNi_{4.6}Sn_{0.4}}$, 69179-15-3; $\mathrm{H_2}$, 1333-74-0.

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Kinetics and Mechanism of the Reaction of Phosphate (H_3PO_4 and $H_2PO_4^-$) with Aquopentaamminechromium(III)

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The reaction of phosphate with $Cr(NH_3)_5H_2O^{3+}$ (pH 1–2) yields the phosphato complex $Cr(NH_3)_5H_2PO_4^{2+}$ which is stable to further reaction (including NH_3 loss) at the temperatures 40–60 °C investigated. From the kinetics (I = 1.00 M ($LiClO_4$)) evidence was obtained for outer-sphere association of H_3PO_4 ($K_1 = 0.32$ M^{-1}) and $H_2PO_4^-$ ($K_2 = 1.8$ M^{-1}) with $Cr(NH_3)_5H_2O^{3+}$, where K_1 and K_2 show little or no dependence on temperature. Rate constants for interchange leading to formation of the phosphato complex are as far as could be ascertained identical ($k_1 = k_2$), with $k(50\ °C) = 1.45 \times 10^{-4}$ s^{-1}, $\Delta H^{\ddagger}$ = 25.0 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = 1.1 cal K^{-1} mol^{-1}. Comparisons are made with other studies involving $Cr(NH_3)_5H_2O^{3+}$ as well as $Cr(H_2O)_6^{3+}$. Reactivity patterns for $Cr(NH_3)_5H_2O^{3+}$ are intermediate between those for $Cr(H_2O)_6^{3+}$ on the one hand (I_a assignment) and $Co(NH_3)_5H_2O^{3+}$ and other 2+ aquo ions on the other (I_d). The previously determined volume of activation for H_2O exchange on $Cr(NH_3)_5H_2O^{3+}$ has been interpreted in terms of an I_a assignment. This is consistent with reactivity patterns only if it is accepted that plots of log k_{aq} against log ($K_{IS}K_{OS}$) yield slopes of 1.0 for an I_d mechanism and <1.0 for an I_a mechanism.

Whereas substitution reactions of $Cr(H_2O)_6^{3+}$ are believed to proceed by an associative interchange (I_a) mechanism,[1] reactions of $Cr(NH_3)_5H_2O^{3+}$ (replacement of H_2O) and Cr^{III}–amine complexes remain controversial with no firm consensus.[2–6] It is now recognized that nonparticipating ligands are relevant in determining the course of a substitution process, and this is particularly well illustrated in the case of cobalt(III) by the assignment of a D mechanism for reactions of $Co(CN)_5H_2O^{2-}$ [7] and I_d for $Co(NH_3)_5H_2O^{3+}$ [8] and with a suggestion of associative character (I_a) for the reactions of $Co(H_2O)_6^{3+}$.[9]

We here report a study of the reaction of phosphate with $Cr(NH_3)_5H_2O^{3+}$, which provides further information and helps clarify some aspects of the substitution behavior of this complex.

Experimental Section

Reactants. The nitrate salt of aquopentaamminechromium(III), $[Cr(NH_3)_5H_2O](NO_3)_3{\cdot}NH_4NO_3$, was first prepared.[10] For the conversion to the perchlorate salt 10 g of the latter was dissolved in 120 mL of water and 72% perchloric acid (60 mL) added.[11] The complex was recrystallized once by using the same procedure. Spectra in 0.10 M $HClO_4$ were in agreement with literature values λ_{max} 481 nm (ϵ 35.3 M^{-1} cm^{-1}) and λ_{max} 361 nm (ϵ 30.5 M^{-1} cm^{-1}).[12,13] A sample of the dihydrogen phosphato complex $[Cr(NH_3)_5(H_2PO_4)](ClO_4)_2{\cdot}2H_2O$ was prepared by the procedure in ref 14. The spectrum in 0.10 M $HClO_4$ gave λ_{max} 502 nm (ϵ 48.4 M^{-1} cm^{-1}) and λ_{max} 370 nm (ϵ 29.3 M^{-1} cm^{-1}) in agreement with published values.[14] Solutions of phosphoric acid were prepared from AnalaR (sp gr 1.75, Hopkin and Williams) reagent. These were standardized by titration with NaOH to the methyl orange end point. Solutions of lithium dihydrogen phosphate were prepared by mixing equivalent volumes of H_3PO_4 and LiOH (BDH, laboratory reagent). Lithium perchlorate was prepared from Li_2CO_3 (BDH, laboratory reagent) and 72% $HClO_4$ (BDH, AnalaR) and was recrystallized three times. Solutions were standardized by passing down an Amberlite IR 120(H) resin column and titrating the liberated H^+ with NaOH.

Determination of Acid Dissociation Constant of H_3PO_4. Solutions of 0.10 M H_3PO_4, I = 1.00 M ($LiClO_4$), were titrated potentiometrically (pH meter Radiometer PHM 4d) with 1.0 M NaOH at three different temperatures. Acid dissociation K_a values obtained were 10^2K_a (M) = 2.05 ± 0.06 (25 °C), 1.72 ± 0.09 (40 °C), and 1.56 ± 0.06 (50 °C). From a graph of log K_a against reciprocal temperature (K) an extrapolated value 10^2K_a = 1.41 ± 0.07 M (60 °C) was obtained. Values obtained were in good agreement with the literature.[15]

Kinetic Runs. Anation reactions (carried out in thermostated spectrophotometric cells) were monitored by conventional spectrophotometry at λ 520 nm (Unicam SP500) (Figure 1). Scan UV–visible spectra (Unicam SP8000) gave retention of isosbestic points at 368, 420, and 470 nm for a run at 60 °C ($[H^+]$ = 0.10 M, I = 1.00 M ($LiClO_4$)), over a 10-h period. Solutions of $Cr(NH_3)_5H_2O^{3+}$ and $Cr(NH_3)_5H_2PO_4^{2+}$ in 0.10 M $HClO_4$ retained constant spectra for at least 8 h at 60 °C. There is thus no evidence for ammonia loss from the phosphato complex. On addition of an excess of H_3PO_4 to $Cr(NH_3)_5H_2O^{3+}$ and heating of the mixture (60 °C), an orange to red color change was observed and the spectrum of $Cr(NH_3)_5H_2PO_4^{2+}$ was obtained. The reaction can be summarized therefore by (1).

$$Cr(NH_3)_5H_2O^{3+} + H_3PO_4 \rightarrow Cr(NH_3)_5H_2PO_4^{2+} + H^+ + H_2O \qquad (1)$$

First-order rate constants, k_{obsd}, were obtained from slopes (×2.303) of plots of absorbance changes log ($A_\infty - A_t$) against time (t), with total phosphate, $[PO_4]_T$, in at least 10-fold excess of $[Cr(NH_3)_5H_2O^{3+}]$. The latter was generally ca. 0.014 M, repeat runs with the concentration decreased 4× giving identical k_{obsd} values. Values of the final absorbance, A_∞, were calculated from the known spectrum of $Cr(NH_3)_5H_2PO_4^{2+}$. Plots were linear to at least 85% completion. Variation of $[H^+]$ was achieved by mixing calculated amounts of LiH_2PO_4, H_3PO_4, and $HClO_4$. The ionic strength was adjusted to 1.00 M ($LiClO_4$) in all cases.

Results

First-order constants, k_{obsd} (Table I), gave a nonlinear dependence on total phosphate, $[PO_4]_T$, at each $[H^+]$ (Figure 2). A reaction scheme (2), which gives (3), is consistent with

$$\begin{tikzcd}
Cr(NH_3)_5H_2O^{3+} + H_3PO_4 \arrow[r, shift left, "K_1"] \arrow[dd, shift right, "K_a"'] & Cr(NH_3)_5H_2O^{3+},H_3PO_4 \arrow[l, shift left] \arrow[dr, "k_1"] & \\
 & & Cr(NH_3)_5(H_2PO_4)^{2+} \quad (2) \\
Cr(NH_3)_5H_2O^{3+} + H_2PO_4 \arrow[r, shift left, "K_2"] \arrow[uu, shift right] & Cr(NH_3)_5H_2O^{3+},H_2PO_4^- \arrow[l, shift left] \arrow[ur, "k_2"'] &
\end{tikzcd}$$

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