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Binding of the Two-Valence-Electron Metal Ions Sc$^+$, Ti^{2+}, and V^{3+} to the Second-Row Hydrides BeH$_2$, BH$_3$, NH$_3$, OH$_2$, and FH: A Computational Study

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We report results from a computational study of the binding in complexes formed from one of the transition-metal ions Sc$^+$, Ti^{2+}, or V^{3+}, each of which has two valence electrons outside an argon core, and one of the second-row hydrides FH, OH$_2$, NH$_3$, BH$_3$, or BeH$_2$. The complexes that involve the electron-rich ligands FH, OH$_2$, and NH$_3$ have strong ion–dipole components to their binding. There are large stabilization energies for σ-interactions that transfer charge from occupied lone-pair natural bond orbitals on the F, O, or N atom of the (idealized) Lewis structure into empty non-Lewis orbitals on the metal ions; these interactions effectively increase electron density in the bonding region between the metal ion and liganded atom, and the metal ions in these complexes act in the capacity of Lewis acids. The complexes formed from the electron-poor hydrides BH$_3$ and BeH$_2$ consistently incorporate bridging hydrogen atoms to support binding, and there are large stabilization energies for interactions that transfer charge from the Be–H or B–H bonds into the region between the metal ion and liganded atom. The metal ions in Sc$^+$–BeH$_2$, Ti^{2+}–BeH$_2$, Ti^{2+}–BH$_3$, and V^{3+}–BH$_3$ act in the capacity of Lewis acids, whereas the scandium ion in Sc$^+$–BH$_3$ acts as a Lewis base.

Introduction

Metal cations bind to neutral ligands such as H$_2$O in a wide variety of physical, chemical, and biological phenomena.[1] For example, approximately one-third of all proteins require a metal ion for their function, and, in many cases, one or more of the surrounding ligands is a water molecule.[2] Novel gas-phase experiments[3–18] and high-level calcula-

tions[19–65] on complexes containing a metal ion and a few neutral ligands have yielded substantial insight into the mechanisms that hold such complexes together; electrostatic effects, the energetic cost of promoting a metal ion to its appropriate bonding state, metal ion–ligand repulsion, and

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dative interactions are some of the factors that influence the overall binding in such moieties.[66] Complexes that contain one or more first-row transition-metal ions are particularly interesting: the (partially) occupied 3d and/or 4s metal-ion orbitals further increase the number of competing binding mechanisms.

The present paper reports results from a computational study of the complexes $M^{n+}-AH_m$, where M^{n+} is one of the first-row transition-metal ions Sc^+, Ti^{2+}, or V^{3+} and AH_m is one of the second-row hydrides FH, OH_2, NH_3, BH_3, or BeH_2. The three metal ions we employed in this study are similar in that they have two valence electrons outside an Ar core and, in accord with Hund's rule, the ground states of their complexes with neutral ligands are usually triplets. However, there are also interesting differences among these metal ions that influence the mechanism(s) by which they bind to neutral ligands. Specifically, the two valence electrons in the triplet ground state of a monovalent scandium ion occupy the 4s and one of the 3d orbitals, whereas in the triplet ground states of the divalent titanium and trivalent vanadium ions both valence electrons occupy 3d orbitals; this difference in orbital occupancy is primarily a result of differences in the shielding of the 4s and 3d electrons in Sc^+ as compared to that in the Ti^{2+} and V^{3+}. (We have not included results from calculations on similar complexes with a net charge greater than +3, e.g., $Cr^{4+}-OH_2$, because the essential integrity of the ligand could not be maintained consistently during the optimizations.) When binding to FH, OH_2, or NH_3, each of which has substantial lone-pair electron density, the metal ions Sc^+, Ti^{2+}, and V^{3+}, with their partially *empty* 3d and/or 4s orbitals, may be expected to act as Lewis acids. On the other hand, when combining with BeH_2 or BH_3, each of which has empty 2p orbitals, these metal ions, with their partially *filled* 3d and/or 4s orbitals, could act as Lewis bases. However, the net positive charge on Sc^+, Ti^{2+}, and V^{3+}, in conjunction with the low electronegativities of the boron and beryllium atoms (2.0 and 1.5, respectively[67]), may be expected to reduce the capacity of these metal ions to donate electron density to the BH_3 or BeH_2 ligands, and their characterization as Lewis acids or bases in these complexes is not evident a priori.

Computational Methods

Ab initio molecular orbital calculations were performed using second-order Møller–Plesset perturbation theory (MP2(FULL)),[68] with the internally stored 6–311++G** basis set;[69–73] the GAUSSIAN 98 suite of programs[74] was used for all the complexes $M^{n+}-AH_m$ ($M^{n+} = Sc^+$, Ti^{2+}, V^{3+}; $AH_m = $ FH, OH_2, NH_3, BH_3, BeH_2).

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Only a single ligand was employed in this study in order to eliminate any ligand−ligand interactions that could mask effects of the metal ion−ligand interactions that we are studying. Complete optimizations were performed on all these complexes and frequency analyses were carried out to confirm that the reported structures are local minima on their MP2(FULL)/6−311++G** potential energy surfaces (PESs), and to determine the thermal corrections necessary for the evaluation of bonding enthalpies at 298 K. (PMP2−0(FULL))/6−311++G** total molecular energies were used for the triplet states.) Since calculations at the MP2(FULL)/6−311++G** level do not always predict the correct electronic configuration for the ground state of some first-row transition-metal complexes,[38,42,47] single-point CCSD(T)(FULL)/6−311++G**// MP2(FULL)/6−311++G** calculations were also performed in order to treat more completely the effects of electron correlation. The CCSD(T) computational level includes a perturbational estimate of connected triple excitations, and calculations at this level generally give reasonable binding energies for transition-metal systems.[47,75,76] For brevity in the main text, calculations at MP2-(FULL)/6−311++G**//MP2(FULL)/6−311++G** and CCSD-(T)(FULL)/6−311++G**//MP2(FULL)/6−311++G** levels will be referred to as "MP2" and "CCSD(T)", respectively. We note that for an isolated Sc$^+$ ion the energy difference for the ^{3}D(sd)−^{3}F(d^2) splitting is 0.75 [0.77] eV at the MP2 [CCSD(T)] computational level; the experimental value for this splitting is 0.60 eV.[42,77] This energy difference is not easy to calculate accurately, and an error of 0.15 [0.17] eV is reasonable.

For each ligand and metal ion, we optimized complexes with several multiplicities, various electronic occupancies, and different initial geometries to increase the likelihood that we located the lowest-energy structures of these complexes. Atomic charges were calculated from natural population analyses (NPA) using the MP2 density.[78−80] The wave functions were analyzed with the aid of natural bond orbitals (NBOs) using the SCF density.[81] In a few cases counterpoise calculations were performed to estimate basis set superposition errors (BSSEs) to our calculated decomposition enthalpies.

Results and Discussion

Total molecular energies, thermal corrections to 298 K, and entropies for the isolated metal ions M^{n+} (M^{n+} = Sc$^+$,

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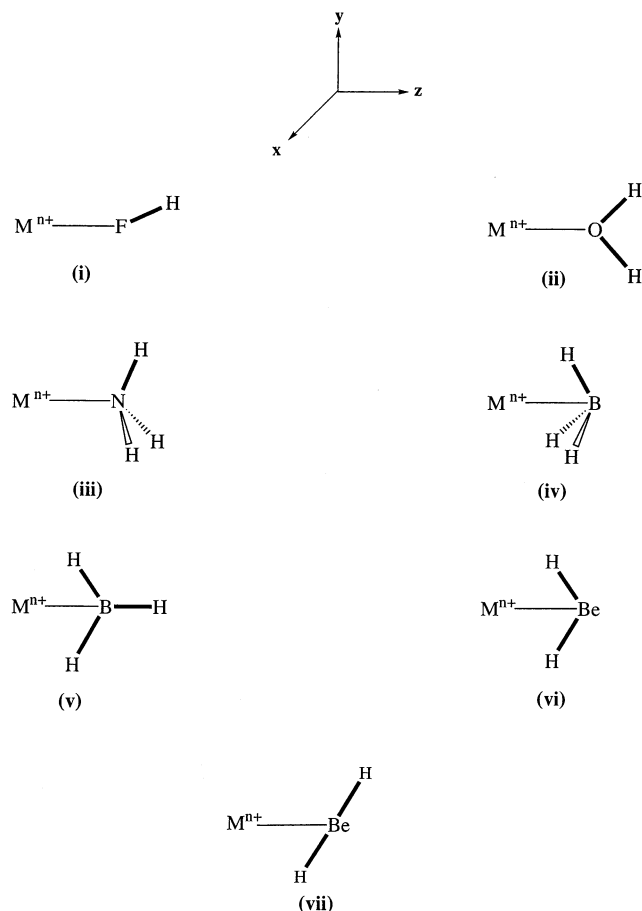
Figure 1. Coordinate system used for the calculations of metal ion−hydride complexes.

Ti^{2+}, V^{3+}), the hydrides AH$_m$ (AH$_m$ = FH, OH$_2$, NH$_3$, BH$_3$, BeH$_2$), and their resulting complexes M^{n+}−AH$_m$ calculated at the MP2 computational level are listed in Table 1S of the Supporting Information; total molecular energies at the CCSD(T) level are listed also in this table. In Figure 1 we show the orientations of the various complexes relative to the coordinate system we employed; these orientations were chosen to facilitate our comparison of orbital occupancies. Selected geometrical parameters for the ground states of these complexes and their decomposition enthalpies at 298 K are listed in Table 1; NPA charges, NPA orbital occupancies, and M^{n+}−A vibrational frequencies calculated at the MP2 computational level are given in Tables 2, 2S, and 3S, respectively.

1. The Complexes M^{n+}−AH$_m$ (M^{n+} = Sc$^+$, Ti^{2+}, V^{3+}; AH$_m$ = FH, OH$_2$, NH$_3$). We first considered complexes of Sc$^+$, Ti^{2+}, and V^{3+} with the hydrides that have substantial lone-pair electron density, FH, OH$_2$, and NH$_3$; their structures are shown schematically in Figure 1i−iii. At the MP2 computational level the ground states of these complexes are triplets, in agreement with a variety of other calculations.[38,42,58,82] The optimized geometries of the metal-ion complexes with H$_2$O and NH$_3$ are such that the dipole

(82) For comparison, we note that the lowest-energy doubly occupied singlet states of Sc$^+$−FH, Sc$^+$−OH$_2$, and Sc$^+$−NH$_3$ are 15.1 [9.9], 11.3 [7.6], and 8.4 [5.3] kcal/mol higher in energy than the corresponding ground states at the MP2 [CCSD(T)] level.

Table 1. Bond Lengths (Å), Bond Angles (deg), and Bonding Enthalpies, $\Delta H°_{298}$ (kcal/mol), for the Complexes $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = FH, OH_2, NH_3, BH_3, BeH_2) Calculated at the MP2(FULL)/6−311++G**//MP2(FULL)/6−311++G** [CCSD(T)(FULL)/6−311++G**//MP2(FULL)/6−311++G**] Computational Levels

A. $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = FH, OH_2, NH_3)

	Sc^+-AH_m (triplet)	$Ti^{2+}-AH_m$ (triplet)	$V^{3+}-AH_m$ (triplet)
AH_m = FH			
$M^{n+}-F$ (Å)	2.201	2.069	1.797
F−H (Å)	0.930	0.946	1.035
∠MFH (deg)	172.1	180.0	180.0
$\Delta H°_{298}$ (kcal/mol)	19.4[a]	45.6	115.9
	[19.6]	[45.2]	[117.6]
AH_m = OH_2			
$M^{n+}-O$ (Å)	2.193	2.056	1.812
O−H (Å)	0.967	0.976	1.031
∠MOH (deg)	127.0	127.6	126.8
$\Delta H°_{298}$ (kcal/mol)	34.3[a]	70.8[a]	182.0
	[34.4]	[70.6]	[185.3]
AH_m = NH_3			
$M^{n+}-N$ (Å)	2.301	2.184	1.910
N−H (Å)	1.022	1.028	1.061
∠MNH (deg)	113.5	114.7	115.0
$\Delta H°_{298}$ (kcal/mol)	40.7[a]	83.8	213.2
	[40.7]	[83.5]	[211.7]

B. $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = BH_3, BeH_2)

	Sc^+-AH_m (singlet)	Sc^+-AH_m (triplet)	$Ti^{2+}-AH_m$ (triplet)	$V^{3+}-AH_m$ (triplet)
AH_m = BH_3				
$M^{n+}-B$ (Å)	2.034	2.202	2.437	2.362
B−H[a] (Å)	1.241[b]	1.234[b]	1.241[b]	1.375[b]
	1.174	1.177	1.174	1.196
∠MHB (deg)	76.6	82.7	92.0	97.4
$\Delta H°_{298}$ (kcal/mol)	48.2	16.5[a]	42.7	164.3
	[39.3]	[19.7]	[42.8]	[170.5]
		(triplet)	(triplet)	(triplet)[f]
AH_m = BeH_2				
$M^{n+}-Be$ (Å)		3.445[c,d]	2.439[e]	
Be−H (Å)		1.365[b,c,d]	1.390[b,e]	
		1.308[c,d]		
∠MHBe (deg)		160.5[c,d]	90.6[e]	
$\Delta H°_{298}$ (kcal/mol)		14.2[c,d]	58.0[e]	
		[14.7][c,d]	[58.8][e]	

[a] $\Delta H°_{298}$ (kcal/mol) evaluated using basis set superposition corrections: Sc^+-FH = 18.4; Sc^+-OH_2 = 32.0; Sc^+-NH_3 = 38.2; $Ti^{2+}-OH_2$ = 68.3; Sc^+-BH_3 = 15.6. [b] Denotes B−H or Be−H distances that involve bridging hydrogen atoms, see Figure 1. [c] Singly hydrogen bridged scandium complex. [d] For the doubly hydrogen bridged scandium complex, the geometrical parameters at the MP2 computational level are Sc^+-Be = 2.247 Å; Be−H = 1.365 Å; ∠ScHBe = 78.8°; the decomposition enthalpy, $\Delta H°_{298}$ is 3.9 kcal/mol. [e] Doubly hydrogen bridged titanium complex. [f] No stable $V^{3+}-BeH_2$ complex could be found at the MP2 computational level.

moments, μ, of the hydrides point directly at the metal cation. Interestingly, the structure of Sc^+-FH is bent at the MP2 computational level, see Table 1, but only to a small extent, ∠$Sc^+-FH \approx 172°$;[83] a linear version of Sc^+-FH is some 8.8 kcal/mol higher in energy. The structures of $Ti^{2+}-$ FH and $V^{3+}-$FH, however, are linear. Thus, the structures of all these complexes with FH, OH_2, and NH_3 are consistent with a strong ion−dipole component to the binding, and this is reflected in their calculated $M^{n+}-A$ distances; e.g., for a given ligand the $M^{n+}-A$ distance decreases as the charge on the metal ion increases ($Sc^+ \rightarrow Ti^{2+} \rightarrow V^{3+}$), see

(83) The structures of some metal ion−hydroxide complexes are also bent.[47]

Table 2. NPA Atomic Charges (e) for the Complexes $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = FH, OH_2, NH_3, BH_3, BeH_2) Calculated at the MP2(FULL)/6−311++G**//MP2(FULL)/6−311 ++G** Computational Level

A. $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = FH, OH_2, NH_3)

	Sc^+-AH_m (triplet)	$Ti^{2+}-AH_m$ (triplet)	$V^{3+}-AH_m$ (triplet)
AH_m = FH[a]			
Q_M	+0.976	+1.964	+2.769
ΔQ_M[b]	+0.024	+0.036	+0.231
Q_F	−0.602	−0.637	−0.568
Q_H	+0.624	+0.673	+0.798
AH_m = OH_2[a]			
Q_M	+0.953	+1.923	+2.520
ΔQ_M[b]	+ 0.047	+ 0.077	+ 0.480
Q_O	−1.008	−1.049	−0.850
Q_H	+0.527	+0.563	+0.665
AH_m = NH_3[a]			
Q_M	+0.930	+1.889	+2.603
ΔQ_M[b]	+0.070	+0.111	+0.297
Q_N	−1.152	−1.211	−1.198
Q_H	+0.407	+0.441	+0.532

B. $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = BH_3, BeH_2)

	Sc^+-AH_m (singlet)	Sc^+-AH_m (triplet)	$Ti^{2+}-AH_m$ (triplet)	$V^{3+}-AH_m$ (triplet)
AH_m = BH_3[a]				
Q_M	+1.614	+1.380	+1.871	+2.374
ΔQ_M[b]	−0.614	−0.380	+0.129	+0.626
Q_B	−0.373	−0.122	+0.427	+0.825
Q_H	−0.121[c]	−0.124[c]	−0.167[c]	−0.162[c]
	0.000	−0.011	−0.036	−0.125
		(triplet)	(triplet)	(triplet)[g]
AH_m = BeH_2[a]				
Q_M		+0.960[d,e]	+1.732[f]	
ΔQ_M[b]		+0.040	+0.268	
Q_{Be}		+1.300[d,e]	+1.546[f]	
Q_H		−0.734[c−e]	−0.639[c,f]	
		−0.526[d,e]		

[a] NPA atomic charges for the isolated hydrides: FH, Q_F = −0.539, Q_H = +0.539; OH_2, Q_O = −0.898, Q_H = +0.449; NH_3, Q_N = −1.028, Q_H = +0.343; BH_3, Q_B = +0.384, Q_H = −0.128; BeH_2, Q_{Be} = +1.188, Q_H = −0.594. [b] ΔQ_M is the electron density transferred to the metal ion. [c] Denotes atomic charges on bridging hydrogen atoms. [d] Singly hydrogen bridged scandium complex. [e] The corresponding charges for the doubly hydrogen bridged scandium complex are Q_M = +0.91; Q_{Be} = +1.296; Q_H = −0.604. [f] Doubly hydrogen bridged titanium complex. [g] No stable $V^{3+}-BeH_2$ complex could be found at the MP2 computational level.

Figure 2A, and for a given metal ion, the $M^{n+}-A$ distance decreases as the calculated dipole moment of the (isolated) hydride increases {NH_3 (1.733 D) → FH (1.969 D) → OH_2 (2.189 D)}.

Since the electronic configuration of the scandium ion involves substantial occupancy of the 4s orbital, we will consider Sc^+-FH, Sc^+-OH_2, and Sc^+-NH_3 separately. The calculated NPA charges for the triplet ground states of these complexes show that there is a net transfer of electron density from each of the ligands to the scandium ion, see Table 2A; the transfer of density is relatively small when F is the liganding atom, 0.02e, but increases to 0.07e for the less electronegative nitrogen atom, see Figure 2B. Furthermore, the NPA charge on the liganding atom in each of these three complexes is more negative than it is in the isolated hydrides, see Figure 2C, resulting in a relatively large net positive charge on the hydrogen atoms; the A−H distances in these complexes are longer and the HOH angles are larger than
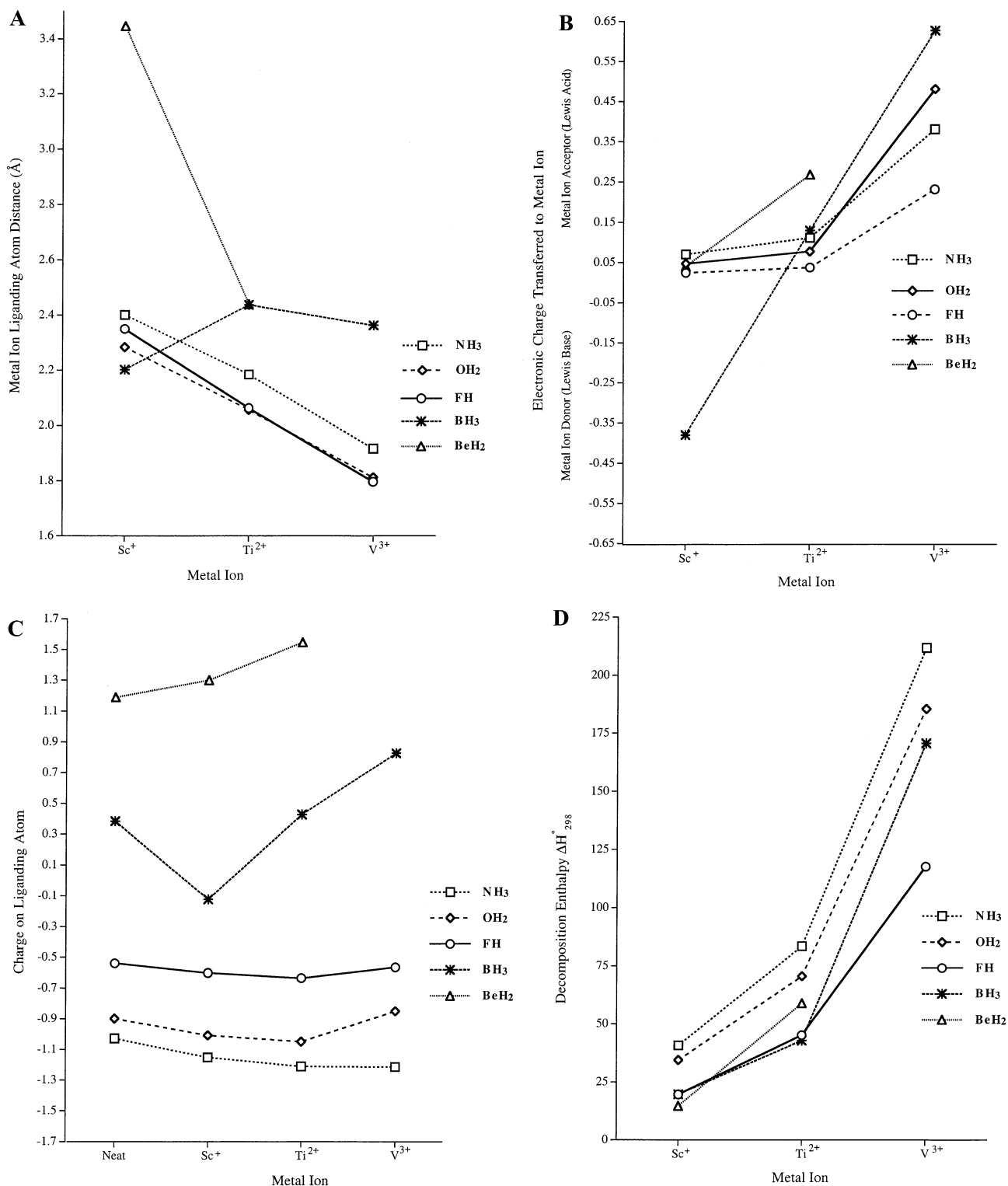
Figure 2. (A) Metal ion–liganding atom distance (Å). (B) NPA electronic charge (e) transferred to the metal ion, calculated from the MP2 density. (C) NPA charge (e) on liganding atom, calculated from the MP2 density. (D) Decomposition enthalpy (kcal/mol) for the lowest-energy triplet states of the metal ion–hydride complexes $M^{n+}–AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = FH, OH_2, NH_3, BH_3, BeH_2) calculated at the CCSD(T) level.

they are in the isolated hydrides, but the distortion energies of these ligands are small, e.g., 0.2 kcal/mol for the water molecule in $Sc^+–OH_2$; HNH angles are smaller.

We can gain valuable insight into the relative importance of the interactions that result in the net transfer of electron density to the scandium ion in these complexes by calculating stabilization energies between various donor–acceptor pairs

of orbitals.[78–81] Second-order perturbative estimates of these stabilization energies, $E(2)$, are given by

$$E(2) = q_i F(i,j)^2/(\epsilon_j - \epsilon_i)$$

where q_i is the donor orbital occupancy, $\epsilon_j - \epsilon_i$ is the difference in orbital energies, and $F(i,j)$ is the off-diagonal

Table 3. Second-Order Stabilization Energies, E(2) (kcal/mol), Orbital Energy Differences, ϵ_j-ϵ_i (a.u.), and Off-Diagonal Fock Matrix Elements, F(i,j) (a.u.), for the Ground States of $M^{n+}-AH_m$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = FH, Oh_2, NH_3) Calculated from the HF/6-311++G** Density

orbitals			Sc⁺−AHₘ (triplet)			Ti²⁺−AHₘ (triplet)			V³⁺−AHₘ (triplet)		
donor (i)	acceptor (j)	spin	E(2)	$\epsilon_j - \epsilon_i$	F(i,j)	E(2)	$\epsilon_j - \epsilon_i$	F(i,j)	E(2)	$\epsilon_j - \epsilon_i$	F(i,j)
AHₘ = FH											
σ_F ($2s - 2p_z$)	σ_M^* ($4s + 3d_{z^2}$)	α	4.26	1.74	0.109	4.98	1.73	0.117	13.31	1.66	0.190
		β	9.15	1.66	0.156	4.68	1.75	0.114	13.42	1.69	0.191
π_F	π_M^*	α	0.66	0.98	0.032	0.86	0.90	0.035	5.03	0.72	0.076
			0.67	0.96	0.032	0.86	0.90	0.035	5.03	0.72	0.076
		β	0.59	1.02	0.031	1.52	0.90	0.047	8.52	0.73	0.099
			0.58	1.02	0.031	1.52	0.90	0.047	8.52	0.73	0.099
σ_M ($4s - 3d_{z^2}$)	σ_F^* ($3s - 3p_z$)	α	7.87	1.14	0.120	a			a		
π_M	π_F^*	α	a			a			a		
			a			a			a		
AHₘ = OH₂											
σ_O ($2s - 2p_z$)	σ_M^* ($4s + 3d_{z^2}$)	α	7.93	1.25	0.126	11.58	1.24	0.151	31.92	1.17	0.246
		β	12.93	1.16	0.155	11.04	1.27	0.149	30.00	1.21	0.242
π_O	π_M^*	α	1.44	0.79	0.043	3.86	0.71	0.066	30.34	0.46	0.149
		β	1.18	0.83	0.040	3.19	0.75	0.062	15.32	0.60	0.121
σ_M ($4s - 3d_{z^2}$)	σ_O^* ($3s - 3p_z$)	α	8.77	1.26	0.133	1.55	1.47	0.060	1.74	1.99	0.074
AHₘ = NH₃			Sc⁺−NH₃			Ti²⁺−NH₃			V³⁺−NH₃		
σ_N ($2s - 2p_z$)	σ_M^* ($4s + 3d_{z^2}$)	α	11.68	0.90	0.130	21.78	0.86	0.172	b	b	b
		β	17.20	0.81	0.149	17.63	0.90	0.159	40.81	0.88	0.240
σ_M ($4s - 3d_{z^2}$)	σ_N^* ($3s - 3p_z$)	α	7.50	1.31	0.125						

^{a} Below threshold value of 0.03 kcal/mol. ^{b} There is a formal V−N bond in this complex.

NBO Fock matrix element that connects the donor (i) and acceptor (j) orbitals. Values of E(2) for a few selected interactions (in the NBO bases) that lead to donation of electron density from the occupied orbitals of the (idealized) Lewis structure into empty non-Lewis orbitals are listed in Table 3.

The net ($\alpha + \beta$) stabilization energy for the σ-interaction that involves the occupied lone-pair ($2s - 2p_z$) orbital on either the F, O, or N atom and the empty ($4s + 3d_{z^2}$) natural hybrid orbital (NHO) on the scandium ion is relatively large, 13.4, 20.9, and 28.9 kcal/mol for Sc^+-FH, Sc^+-OH_2, and Sc^+-NH_3, respectively; these values increase as the electronegativity of the liganding atom decreases, primarily as a result of a decrease in the energy separation between the two orbitals involved, see Table 3. This σ-interaction in these complexes effectively increases electron density in the bonding region between the scandium ion and the liganding atom, although none of the NBOs is classified as a Sc−A formal bonding orbital. Nevertheless, the relative magnitudes of the σ-stabilization energies in these scandium hydrides are reflected in their enthalpies for decomposition into Sc^+ and FH, OH_2, or NH_3, 19.6, 34.4, and 40.7 kcal/mol, respectively at the CCSD(T) computational level, see Figure 2D. The net stabilization energy for a π-interaction in Sc^+-OH_2 that transfers charge from the occupied out-of-plane $2p_x$ orbital on the oxygen atom to the empty ($3d_{xz} + 4p_x$) NHO on the scandium ion is comparatively small, 2.6 kcal/mol, as is the net stabilization energy from the two π-interactions in Sc^+-FH, 2.5 kcal/mol. There are also interactions that transfer electron density from the hydride F−H, O−H, or N−H bonding orbitals into various 3d orbitals on the scandium ion, but the values of E(2) for these

interactions are small, 1.0, 3.5, and 5.1 kcal/mol, respectively, see Table 4S. Interestingly, interactions that transfer charge from the metal ion to the ligand, i.e., "back-donation", are significant in these complexes. For example, the values of E(2) for the interaction between the occupied ($4s - 3d_{z^2}$) lone-pair α-NHO on the scandium ion and an empty ($3s - 3p_z$) orbital on the F, O, or N atoms in Sc^+-FH, Sc^+-OH_2, and Sc^+-NH_3 are 7.9, 8.8, and 7.5 kcal/mol, respectively, see Table 3. Nevertheless, in these hydride complexes the dominant role of the scandium ion is as a Lewis acid.

For the complexes $Ti^{2+}-OH_2$ and $V^{3+}-OH_2$, the $3d_{x^2-y^2}$ and $3d_{yz}$ natural atomic orbitals (NAOs) on the metal ions are occupied for the orientation in Figure 1ii. The $3d_{x^2-y^2}$ orbital, however, is mixed with the $3d_{z^2}$ orbital ($3d_{x^2-y^2} - 3d_{z^2}$), similar to the ($4s - 3d_{z^2}$) hybridization we observed in Sc^+-OH_2. There is a relatively small transfer of electron density from the water ligand to the titanium ion, 0.08e, but the transfer to the vanadium ion is much larger, 0.48e, see Figure 2B.[84] In $Ti^{2+}-OH_2$ and $V^{3+}-OH_2$ the net stabilization energies for the σ-interaction between the in-plane occupied lone-pair ($2s - 2p_z$) orbital on the oxygen atom and the empty ($4s + 3d_{z^2}$) NHO on the metal ion are large, 22.6 and 61.9 kcal/mol, respectively; the corresponding values of E(2) for the π-interaction involving the out-of-plane $2p_x$ lone-pair orbital on the oxygen atom and the empty ($3d_{xz} + 4p_x$) NHO on the metal ion are smaller, 7.0 and 45.7 kcal/mol, respectively. No formal metal−oxygen bonding orbital is identified among the NBOs in either of these hydrates.

(84) It may be noted that $V^{3+}-OH_2$ is the only complex involving the electron-rich ligands for which the calculated charge on the liganding atom is less negative than it is for the isolated hydride, see Figure 2C.

Stabilization energies for charge transfer from O−H bonding orbitals in Ti^{2+}−OH_2 and V^{3+}−OH_2 to 3d orbitals on Ti^{2+} or V^{3+} are relatively small, 0.7 and 6.1 kcal/mol, respectively, see Table 4S. Interactions that lead to back-donation from Ti^{2+} and V^{3+} to the water molecule in these two complexes have stabilization energies of only 1.5 and 1.8 kcal/mol, respectively, and for these hydrates the metal ions behave primarily as Lewis acids. In accord with the particularly large σ- and π-stabilization energies noted above in V^{3+}−OH_2, the enthalpy change for the decomposition of this complex into V^{3+} and OH_2 is extremely large, 185.3 kcal/mol at the CCSD(T) level; the corresponding value for Ti^{2+}−OH_2 is smaller, 70.6 kcal/mol, see Table 1. (Values of $\Delta H°_{298}$ for alternative decomposition routes are given in Table 5S.)[85]

The two valence electrons on the metal ions in the ground states of Ti^{2+}−FH, Ti^{2+}−NH_3, V^{3+}−FH, and V^{3+}−NH_3 are distributed among the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, and $3d_{x^2-y^2}$ NAOs, see Table 2S; the NHOs are combinations of the $3d_{xz}$ and $3d_{xy}$ as well as of the $3d_{yz}$ and $3d_{x^2-y^2}$ NAOs. In each of these four complexes there is a net transfer of electon density to the metal ion, see Table 2A. Interestingly, one of the α-NBOs in V^{3+}−NH_3 is classified as a V−N bonding orbital; it combines the occupied lone-pair $(2s - 2p_z)$ orbital on the nitrogen atom and the $(4s + 3d_{z^2})$ NHO on the vanadium ion $(0.59NHO_V + 0.80NHO_N)$. The corresponding β-NBO in V^{3+}−NH_3 is classified as a nitrogen lone-pair orbital, but it interacts strongly with the unoccupied $(4s + 3d_{z^2})$ orbital on V^{3+}: the stabilization energy is 40.8 kcal/mol. None of the NBOs involving the metal ions in Ti^{2+}−NH_3, V^{3+}−FH, or Ti^{2+}−FH are classified as bonding, but there are strong donor−acceptor interactions similar to that noted above for the β-NBO in V^{3+}−NH_3, see Table 3. The net value of $E(2)$ for the π-interaction in V^{3+}−FH, 27.1 kcal/mol, is about five times larger than the corresponding value in Ti^{2+}−FH, 4.8 kcal/mol. The total stabilization energy for charge transfer from either the F−H or the N−H bonding orbitals to various empty 3d orbitals on the trivalent vanadium ion is approximately 10 kcal/mol, see Table 4S. Back-donation is not very important in these hydrogen fluoride and ammonia complexes, and the titanium and vanadium ions again act predominantly as Lewis acids.

Since the ground state of Sc^+−OH_2 involves significant occupancy of the 4s orbital, whereas the ground states of Ti^{2+}−OH_2 and V^{3+}−OH_2 do not, we calculated various donor−acceptor stabilization energies for the common excited state of these hydrate complexes in which the valence electrons of the metal ions occupy the $3d_{xy}$ and $3d_{yz}$ NAOs; the results are listed in Table 6S. There is a net transfer of electron density, 0.01e, 0.08e, and 0.50e, from the water ligand to the metal ion in these excited states of Sc^+−OH_2, Ti^{2+}−OH_2, and V^{3+}−OH_2, respectively; none of the NBOs are classified as metal−oxygen bonding orbitals. The stabilization energies for the σ- and π-interactions that involve electron donation from the in-plane and out-of-plane lone-pair orbitals on the water molecule in these complexes to the various metal ions both *increase* as the formal charge

on the metal ion *increases* ($Sc^+ \rightarrow Ti^{2+} \rightarrow V^{3+}$); this increase is a result of both smaller orbital energy differences and larger Fock matrix elements. With the exception of V^{3+}−OH_2, stabilization energies for the π-interactions are smaller than those for the σ-interactions. Furthermore, stabilization energies for back-donation are relatively small in these hydrate excited states and, as in the ground states, the metal ions act primarily as Lewis acids.

2. The Complexes M^{n+}−AH_m (M^{n+} = Sc^+, Ti^{2+}, V^{3+}; AH_m = BH_3, BeH_2). The ground states of the complexes involving Sc^+, Ti^{2+}, or V^{3+} and either of the hydrides BH_3 or BeH_2 are also usually triplets at the MP2 and CCSD(T) computational levels. The only exception is Sc^+−BH_3, where a singlet state is 8.1 [7.2] kcal/mol *lower* in energy than the lowest-energy triplet state; for comparison, we note that the corresponding singlet state of Ti^{2+}−BH_3 is nearly 40 kcal/mol *higher* in energy than its triplet ground state. Unlike the electron-rich hydrides FH, OH_2, or NH_3, which have large permanent dipoles and where the NPA charges on the F, O, and N atoms are negative, the (planar) boron and (linear) beryllium hydrides have no permanent dipoles and the charges on the B and Be atoms are positive, see Table 2. Thus, it is not surprising that the optimized structures of M^{n+}−BH_3 and M^{n+}−BeH_2 are quite different from those of the corresponding ammonia and water complexes. The lowest-energy forms of the BH_3 and BeH_2 complexes have at least one of the (negatively charged) hydrogen atoms in a bridging position. The distance between the metal ion and the B or Be atom in these complexes is generally longer than the distance between the metal ion and the N or O atoms in the analogous ion−dipole complexes involving NH_3 or OH_2, see Figure 2A; the only exception is for Sc^+−BH_3, where the distance between Sc and B is relatively short (vide infra).

We initially optimized a triplet state structure of Sc^+−BH_3 where the starting geometry (C_{3v}) was similar to that of the corresponding ammonia complex. During the optimization the borane inverted, moving all three hydrogen atoms into bridging positions, where the Sc−B−H angle is 78.8°, see Figure 1iv. This triply bridged form of Sc^+−BH_3, however, is not the lowest-energy form of this complex on the triplet-state PES; a doubly bridged (slightly puckered) structure is 6.1 [8.1] kcal/mol *lower* in energy, see Figure 1v. In this form of Sc^+−BH_3, the scandium ion *loses* 0.38e of electron density, to the borane ligand. This transfer of charge reverses the sign of the NPA charge on the boron atom from +0.38e in isolated BH_3 to −0.12e in Sc^+−BH_3; each of the two bridging hydrogen atoms is also negatively charged, −0.12e, see Table 2B. Interestingly, a scandium−boron π-like bonding orbital ($0.62NHO_{Sc} + 0.78NHO_B$) that uses the empty $2p_x$ orbital on boron is found among the α-NBOs in this complex.[86] The metal ions in the analogous doubly bridged (planar) forms of Ti^{2+}−BH_3 and V^{3+}−BH_3 *gain* 0.13e and 0.63e of electron density, respectively, from the borane ligand. No metal ion−boron π-bonding orbitals

(85) Corongiu, G.; Clementi E. *J. Chem. Phys.* **1978**, *69*, 4885−4887.

(86) In the planar form of this doubly bridged complex, which is a first-order TS, the Sc−B π-bond involves the filled $(3d_{xz} + 4p_x)$ α-NHO on Sc^+ and the empty $2p_x$ orbital on boron.

Table 4. Net Second-Order Stabilization Energies, $E(2)$ (kcal/mol), for $M^{n+}-AH_m$ (M^{n+} = Sc^+,Ti^{2+},V^{3+}; AH_m = BH_3, BeH_2)

	orbitals			Sc^+-AH_m $E(2)$		$Ti^{2+}-AH_m$ $E(2)$		$V^{3+}-AH_m$ $E(2)$
	donor (i)	acceptor (j)	spin	(singlet)	(triplet)	(singlet)	(triplet)	(triplet)
$AH_m = BH_3$	B−H	LP_M* [b]	α	102.30 (50.20)[a]	32.72 (18.16)[a]	80.80 (44.86)[a]	28.00 (17.28)[a]	34.70 (34.70)[a]
			β		31.98 (18.66)[a]		24.50 (15.13)[a]	53.02 (27.91)[a]

| | orbitals | | | (triplet) | | (triplet) | | |
	donor (i)	acceptor (j)	spin	singly bridged	doubly bridged	doubly bridged		
$AH_m = BeH_2$	Be−H	LP_M*[b]	α	8.13 (6.40)[a]	40.60 (25.32)[a]	52.96 (32.77)[a]		
			β	14.60 (10.55)[a]	34.82 (20.68)[a]	43.82 (27.82)[a]		

[a] Stabilization energy transferred to ($4s + 3d_{z^2}$) orbital on the metal ion. [b] LP_M* is the unoccupied lone pair 3d orbital on the metal ion.

are found among the NBOs in these two complexes, and the net stabilization energies for interactions that transfer charge from occupied 3d lone-pair orbitals on the titanium and vanadium ions to the empty $2p_x$ orbital on the boron atoms are only 4.2 and 1.7 kcal/mol, respectively. Thus, the large positive charge on the titanium and vanadium ions reduces their capacity to act as electron donors. In all three of these doubly bridged borane complexes there are large stabilization energies, 64.7, 52.5, and 87.7 kcal/mol, for interactions that lead to charge transfer from B−H bonding orbitals to various 3d metal-ion orbitals in Sc^+-BH_3, $Ti^{2+}-BH_3$, and $V^{3+}-BH_3$, respectively, see Table 4. A significant portion of these stabilization energies, 56.8%, 62.9%, and 71.5%, respectively, are associated with interactions that transfer charge to the ($4s + 3d_{z^2}$) orbital on the metal ion. This transfer increases electron density in the region between the metal ion and boron atom, although none of the NBO orbitals are classified as metal ion−boron σ-bonding orbitals. In Sc^+-BH_3, the transfer of charge from the borane ligand to the metal ion does not compensate for the electron density that is assigned to the boron atom as a result of the Sc−B π-bond, and the dominant role of the scandium ion in this complex is as a Lewis base. In contrast, the dominant roles of the titanium and vanadium ions in $Ti^{2+}-BH_3$ and $V^{3+}-BH_3$ are as Lewis acids. The decomposition enthalpies of the doubly bridged, triplet states of Sc^+-BH_3 and $Ti^{2+}-BH_3$, 19.7 and 42.8 kcal/mol, are about 50% of the corresponding decomposition enthalpies of Sc^+-NH_3 and $Ti^{2+}-NH_3$, 40.7 and 83.5 kcal/mol, respectively. On the other hand, the decomposition enthalpy of $V^{3+}-BH_3$, 170.5 kcal/mol, is over 80% of the corresponding value for $V^{3+}-NH_3$, 211.7 kcal/mol, despite the presence of a V−N σ-bonding orbital among the α-NBO in this latter complex. The relatively large decomposition enthalpy of $V^{3+}-BH_3$ is partially a consequence of bonding between the vanadium ion and the bridging hydrogen atoms, e.g., both B−H$_{bridging}$ and V−H$_{bridging}$ bonding orbitals are found among the NBOs in $V^{3+}-BH_3$, suggesting that this complex can be described as a $[V-H_2BH]^{3+}/[VH_2-BH]^{3+}$ hybrid structure.

As noted above, a singlet state of Sc^+-BH_3 is lower in energy than any of the triplet states we found at both the MP2 and CCSD(T) computational levels. The structure of this singlet complex is doubly hydrogen-bridged (slightly puckered), similar to that of the lowest-energy triplet state;

the Sc−B distance, however, is some 0.17 Å shorter while the bridging B−H distances are 0.04 Å longer, suggesting a stronger metal ion−boron interaction in the singlet state than in the triplet state. The decomposition enthalpy for the singlet state of this complex, 39.3 kcal/mol, is nearly double that for the corresponding triplet state, 19.7 kcal/mol, at the CCSD(T) level. The calculated atomic charges for this singlet state of Sc^+-BH_3 clearly show that the scandium ion acts as a Lewis base, donating more than 0.60e of electron density to the BH_3 ligand, see Table 2; the boron atom in this complex carries a substantial negative charge, −0.37e, as do the bridging hydrogen atoms, −0.12e. The NBO analysis of this singlet complex identifies an Sc−B π-like bonding orbital ($0.77NHO_{Sc} + 0.64NHO_B$), similar to the corresponding bonding orbital found in the triplet state. There is a large net stabilization energy, 102.3 kcal/mol, associated with interactions that donate charge from the bridging B−H bonding orbitals into various lone-pair 3d orbitals on the scandium ion. Nearly 50% of this stabilization energy comes from the interaction that donates charge into the ($4s + 3d_{z^2}$) orbital on the scandium ion; this interaction effectively increases electron density in the region between Sc^+ and B, but no formal scandium−boron σ-bond is found in the NBO analysis.

Optimized triplet-state structures for the beryllium hydride complexes Sc^+-BeH_2 and $Ti^{2+}-BeH_2$ were found in which both hydrogen atoms are in bridging positions, see Figure 1vi; several attempts at locating the analogous structure of $V^{3+}-BeH_2$ failed to yield a stable complex. The structure of the scandium complex is slightly puckered, while that of the titanium complex is planar. The BeH_2 moiety in each of these complexes is severely bent, e.g., ∠HBeH is 129.7° and 109.3° for Sc^+-BeH_2 and $Ti^{2+}-BeH_2$, respectively, which results in relatively large distortion energies for this moiety, 13.6 and 28.1 kcal/mol. The scandium and titanium ions in these complexes gain electron density, 0.04e and 0.27e, respectively, from the beryllium hydride ligand. A Sc−Be π-bonding orbital ($0.93NHO_{Sc} + 0.36NHO_{Be}$) that involves the empty $2p_x$ orbital on Be is found among the NBOs of Sc^+-BeH_2; no such bonding orbital is found in $Ti^{2+}-BeH_2$, and the net stabilization energy for interactions that transfer charge from occupied 3d lone-pair orbitals on Ti^{2+} to the empty $2p_x$ orbital on Be is only 0.4 kcal/mol. There are large stabilization energies, 75.4 and 96.8 kcal/mol, for interactions

that lead to charge transfer from Be−H bonding orbitals to various 3d lone-pair orbitals on the scandium and titanium ions respectively in these complexes, and more than 60% of these stabilization energies are due to interactions that transfer charge into the region between the metal ion and the beryllium atom. The overall transfer of charge to the scandium ion from the various orbitals on the BeH_2 moiety in $Sc^+−BeH_2$ more than compensates for the charge density assigned to the beryllium atom from the Sc−B π-bonding orbital, and the scandium ion acts as a weak Lewis acid; the distribution of charge density in $Ti^{2+}−BeH_2$ clearly shows that the titanium ion in this complex acts as a much stronger Lewis acid. Despite the π-bonding α-NBO of $Sc^+−BeH_2$, the value of $\Delta H°_{298}$ for its decomposition into Sc^+ and BeH_2 is quite small, 3.9 kcal/mol; the decomposition enthalpy of $Ti^{2+}−BeH_2$ is much larger, 58.0 kcal/mol. The large decomposition enthalpy of $Ti^{2+}−BeH_2$ appears to be the result of a relatively strong electrostatic attraction between the titanium ion and the two bridging hydrogen atoms.

Although we were not able to find any conformer of $Ti^{2+}−BeH_2$ which was lower in energy than its doubly hydrogen bridged form described above, a singly hydrogen bridged structure of $Sc^+−BeH_2$ proved to be 9.4 [8.9] kcal/mol lower in energy than its doubly bridged form at the MP2 [CCSD-(T)] computational level, see Figure 1vii; the analogous singly bridged form of $Ti^{2+}−BeH_2$ is 8.5 kcal/mol *higher* in energy than the doubly bridged form. This singly bridged $Sc^+−BeH_2$ complex is planar, the BeH_2 moiety is nearly linear (∠HBeH 175.1°), which results in a negligible distortion energy, and the Sc−$H_{bridging}$ distance, 2.128 Å, is much longer than the Be−$H_{bridging}$ distance, 1.365 Å; the scandium−beryllium distance in this structure is extremely large 3.445 Å, and this reduces the electrostatic repulsion between the positively charged scandium, +0.96e, and beryllium, +1.30e. There is a net transfer of only 0.04e electron density to the scandium ion in this form of $Sc^+−BeH_2$; no Sc−Be bonding orbital is found among the NBOs. The bridging hydrogen atom, which has the largest negative charge of any hydrogen atom in this study, −0.73e, provides a strong electrostatic attraction in this complex. There is a substantial stabilization energy, 22.7 kcal/mol, for interactions that transfer charge from the two Be−H bonding orbitals to lone-pair 3d orbitals on the scandium ion; 75% of this stabilization energy involves charge transfer into the (4s + $3d_{z^2}$) orbital, and 96% of this originates from the bridging Be−H orbital. Although the decomposition enthalpy for this form of $Sc^+−BeH_2$ is small, 14.2 [14.7] kcal/mol at the MP2 [CCSD(T)] level, it is some 10 kcal/mol larger than that found for the doubly hydrogen bridged form.

Conclusions

The ground state of each of the complexes $M^{n+}−FH$, $M^{n+}−OH_2$, and $M^{n+}−NH_3$ (M^{n+} = Sc^+, Ti^{2+}, V^{3+}), in which the ligand has at least one lone pair of electrons, is found consistently to be a triplet state. There is a strong ion−dipole component to the binding in these hydride complexes: for a given ligand, the $M^{n+}−A$ distance decreases and the value of the decomposition enthalpies increases as the formal

charge on the metal ion increases ($Sc^+ \rightarrow Ti^{2+} \rightarrow V^{3+}$); for a given metal ion, the $M^{n+}−A$ distance decreases and the decomposition enthalpy increases as the dipole moment of the isolated hydride increases. We also note that, for a given metal ion, the decomposition enthalpy of the complex increases as the electronegativity of the liganded atom decreases and the transfer of electron density to the metal ion increases. In each of these complexes there is a large net stabilization energy for the σ-interaction that transfers charge into the bonding region between the metal ion and the liganding atom; the magnitude of this stabilization energy increases as the formal charge on the metal ion increases. Stabilization energies for σ-interactions in $M^{n+}−OH_2$ and $M^{n+}−FH$ are generally smaller in magnitude than those for σ-interactions. Except for $V^{3+}−NH_3$, no formal $M^{n+}−A$ bonding orbitals are found in the NBO analyses of these complexes. Stabilization energies for interactions that result in a transfer of electron density from occupied orbitals on the metal ion to empty orbitals on the ligand are relatively small (particularly for titanium and vanadium), and the metal ions in these complexes that involve electron-rich ligands act primarily as Lewis acids.

The ground states of the complexes $M^{n+}−BH_3$ and $M^{n+}−BeH_2$ (M = Sc^+, Ti^{2+}, V^{3+}) are also usually triplets, although the lowest-energy state of $Sc^+−BH_3$ is a singlet. The structures of these boron and beryllium hydride complexes involve one or more bridging hydrogen atoms. The lowest-energy triplet and ground singlet states of $Sc^+−BH_3$ are doubly hydrogen bridged and exhibit π-bonding, and the scandium ion *loses* substantial electron density to the borane ligand; this is the only complex in which the metal ion acts primarily in the capacity of a Lewis base. The lowest-energy forms of $Ti^{2+}−BH_3$ and $V^{3+}−BH_3$ are also doubly hydrogen bridged, but the large positive charges on the titanium and vanadium ions reduce their capacity to donate electron density to the weakly electronegative boron atom, and in these complexes the metal ions act primarily as Lewis bases. The structure of $Ti^{2+}−BeH_2$ is also doubly hydrogen bridged at the MP2 computational level, and there is an overall transfer of 0.27e of electron density to the titanium ion, which clearly acts as a Lewis acid. On the other hand, the lowest-energy triplet state structure of $Sc^+−BeH_2$ is singly hydrogen bridged with very little transfer of charge to the scandium ion; the binding in this complex involves a strong electrostatic attraction between the scandium cation and the negatively charged bridging hydrogen atom. In all the BH_3 and BeH_2 complexes we studied, there are interactions that stabilize these complexes by delocalizing electron density from the B−H or Be−H bonding regions to the region between the metal ion and the boron or beryllium atoms.