Table I.[a] Thermochemical Data for First-Row Transition-Metal Hydrates, Hydroxides, Oxides, and Hydrides

M^+	$D(M^+—OH_2)$[b]	$D(M^+—OH)$[b]	E_p[c]	$D_0(M^+=O)$[d]	$D_0(M^+—H)$[e]	$E(H—M^+—OH)$[f]	$E(H—M^+=O)$[f]	$D(M^+O—H)$[f]
K^+	17.0[g]							
Ca^+	29.0[h]	106[i]		58[i]	45.9[d]	34	3	149
Sc^+	31.4	87.8	19.1	159	55.3	25	113	30
Ti^+	38.0	113	16.1	161	55.1	50	115	53
V^+	36.2	107	15.2	131	47.3	36	77	71
Cr^+	29.0	74.3, 73[j]	25.3	85	27.7	−16	12	90, 89
Mn^+	32.5	82	26.5	57	47.5	12	3	127
Fe^+	28.8	85.3, 76,[k] 77,[l] 73[m]	20.6	69	47.0	14, 5, 6, 2	15	117, 108, 109, 105
Co^+	37.1	72.2, 71[l]	29.2	64	45.5	0	8	109, 108
Ni^+	36.5	42.2	31.9	45	38.5	−37	−18	98
Cu^+	35.0				21.8			
Zn^+	39.0	30.4			53.3			

[a] All values in kcal/mol. [b] This work except where noted. Average standard deviation in about a dozen measurements for each ion, ±3 kcal/mol; this is also believed to be the accuracy of the method.[2] [c] The promotion energy.[13] [d] Reference 8, with ±3–7 kcal/mol uncertainty. [e] Reference 3, ±2–4 kcal/mol. [f] Assuming reformation of the O—H bond and using $D_0(H—OH)$ = 118 kcal/mol and $D_0(O—H)$ = 101 kcal/mol from *JANAF Thermochemical Tables*, 2nd ed.; NSRDS-NBS 37; National Bureau of Standards: Washington, DC, 1971. [g] Reference 4a. [h] Reference 4b. [i] Murad, E. *J. Chem. Phys.* **1981**, *75*, 4080. [j] Reference 8. [k] Reference 9, ±4.6 kcal/mol. [l] Reference 7, ±6 kcal/mol. [m] Reference 7, ±3 kcal/mol.

Having established the hydroxyl bond energies, we can estimate the energies $E(H—M^+—OH)$ needed for removal of H_2O from $H—M^+—OH$ ions for all M^+ except Ti^+ (Table I). These disagree strongly with our measured H_2O binding energies, except in the case of V^+ and possibly Ca^+ and Sc^+. We conclude that our ions have the structure $M^+—OH_2$, with the possible exceptions of $M^+ = Ca^+$ to V^+.

The hydroxyl binding energies of the transition-metal cations vary strongly and show a tendency to decrease for late transition metals. The water binding energies fall into two groups: the values for Sc^+, Cr^+, Mn^+, and Fe^+ are near 30 kcal/mol, the others near 37 kcal/mol; this is hard to attribute to variations in the ionic radius. Detailed understanding of the $D(M^+—OH)$ and $D(M^+—OH_2)$ values requires elaborate calculations similar to those published[12] for the $M^+—H$ bond. We merely note the existence of an approximate linear correlation between the $M^+—OH$ bond energies and promotion energies[13] (Figure 1). The correlation suggests that early transition-metal ions have a propensity to use their 3d orbitals, whereas the late ones prefer to utilize the 4s orbital for bonding, as demonstrated previously[12] for $M^+—H$ bonds.

Our value of the hydration energy $D(Fe^+—OH_2)$ = 28.8 kcal/mol conflicts with the previous estimate[6a] $D_0(Fe^+—CO)$ = 37.6 kcal/mol, since H_2O readily displaces CO in Fe^+CO at low pressure and room temperature.[14] The reported value of $D_0(Fe^+—C_2H_4)$ = 34 ± 2 kcal/mol[15] also contradicts the earlier estimate,[6a] since C_2D_4, too, displaces CO in Fe^+CO.[14]

The Cu^+ ion binds a second water molecule somewhat more strongly (39 kcal/mol) than the first one (35 kcal/mol).[2] We have now measured the second hydration energies also for Fe^+ (38 kcal/mol), Co^+ (45 kcal/mol), and Ni^+ (38 kcal/mol). These can be compared with the first hydration energies of 29, 37, and 37 kcal/mol, respectively. Monopositive ions of first-row transition metals thus may have a general tendency to attach a second water ligand at least as strongly as the first one. Along with the variation in the first hydration energies across the series, this is indicative of some degree of dative bonding, distinct from the presumably purely electrostatic bonding between water and alkali[4a] or alkaline earth[4b] cations. In these, the first hydration energy is dictated by the ionic radius, and the second hydration energy is several kcal/mol smaller than the first one as a result of unfavorable electrostatic ligand–ligand interactions.

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Registry No. Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; H_2O, 7732-18-5.

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Sequential Solvation of Atomic Transition-Metal Ions. The Second Solvent Molecule Can Bind More Strongly Than the First

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We wish to report the determination of sequential water and ammonia solvation energies for the series of first-row transition-metal atomic ions V^+, Cr^+, Mn^+, Fe^+, Co^+, and Ni^+. A remarkable trend is found wherein for most metals the second solvent binding energy significantly exceeds the first. This is a striking departure from the normal *decrease* in successive solvent binding energies of all other atomic ions for which data are available.[1]

Atomic transition-metal ions are generated by dissociative electron ionization and Penning ionization of volatile metal carbonyl complexes in the helium flow reactor of a flowing afterglow–triple quadrupole apparatus.[2] Termolecular association reactions of the metal ions with added H_2O or NH_3 vapor produce a kinetic mixture of thermalized $M^+(H_2O)_n$ (n = 1–3) and $M^+(NH_3)_n$ (n = 1–4) cluster ions. Unimolecular and bimolecular reactions of mass-selected cluster ions are carried out in the central quadrupole of the triple quadrupole analyzer, where both pressure and kinetic energy effects can be characterized.

The thermochemistry for sequential solvation of the atomic metal ions by H_2O and NH_3 can be estimated from the translational energy thresholds for collision-induced dissociation (CID) of the corresponding cluster ions with argon target gas.[3] Figure

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(3) $P(Ar) \leq 5 \times 10^{-5}$ Torr (single-collision conditions); reactant ion retarding potential analysis locates the energy origin and shows a typical kinetic energy distribution of 0.8–1.3 eV (fwhm, lab frame).

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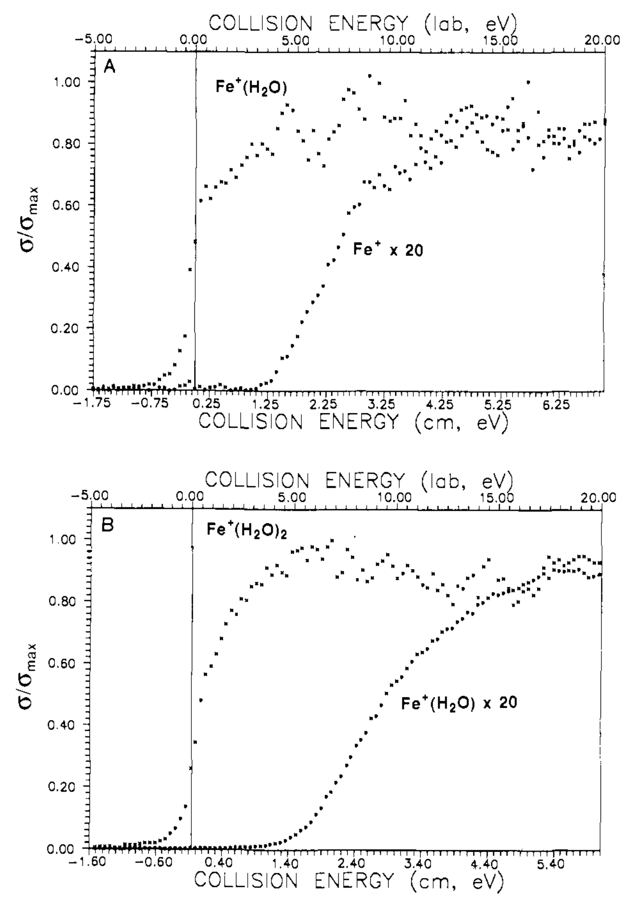

Figure 1. Plot of reactant ion transmission curves (X) and normalized cross sections (*) for dissociation of $Fe^+(H_2O)_{1,2}$ cluster ions versus center-of-mass collision energy (eV). Argon target gas at 4×10^{-5} Torr; reactant ion energy distributions 1.0 eV fwhm (lab frame): (A) Fe^+ from $Fe^+(H_2O)$, estimated threshold energy 1.48 eV; (B) $Fe^+(H_2O)$ from $Fe^+(H_2O)_2$, estimated threshold energy 1.79 eV.

1 presents a plot of the normalized cross sections (σ/σ_{max}) for two dissociation reactions of $Fe^+(H_2O)_{1,2}$ cluster ions versus the center-of-mass collision energy. Estimates of the threshold dissociation energies were obtained from the appearance plots by a fitting procedure that is described in previous reports from this laboratory.[4-7] For the data sets shown in Figure 1, threshold energies of 1.48 eV (34.1 kcal/mol) and 1.79 eV (41.2 kcal/mol) are obtained for the first (Figure 1A) and second (Figure 1B) H_2O ligand dissociation energies, respectively.

Table I provides a summary of results for the six transition-metal ions, along with data for a few other atomic and small polyatomic ions. The first and second H_2O and NH_3 binding energies could be determined for each of the transition-metal ions; the third solvent binding energy is typically much lower than the first two and could be reliably estimated in only a few cases. The most outstanding feature in the transition-metal ion data is the relative magnitudes of the dissociation energies. For the hydrate series, the second H_2O binding energy is greater than the first in every case except Mn^+ where a substantial decrease occurs (8.7 kcal/mol). The same type of behavior is displayed in the ammine series for all metals except V^+ where a monotonic decrease in successive NH_3 binding energies occurs through the fourth cluster. It is of interest to note that while the Mn^+ ion also exhibits a decreased affinity for the second NH_3 molecule compared to the first, the difference is much less than that found with water.

These results represent an unprecedented departure from the solvation energy trends established for all other atomic ions for which data are available in the literature.[1] Alkali metal ions, rare earth metal ions, and halide negative ions all exhibit progressively decreasing energies of binding to water, ammonia, and other small molecules. Sequential H_2O binding energies for Ag^+ are also known; these too display the "normal" ordering.[8] Simple electrostatic models satisfactorily account for this general behavior, i.e., charge dispersal and/or intraligand steric effects accrue with the addition of each new solvent molecule, thereby reducing the successive interaction energies in the growing cluster ion.[9]

We consider three possible origins of the anomalous solvation energy orderings found for the transition-metal ions. First, it is important to recognize that ion appearance measurements are kinetic experiments and that our threshold energies are actually upper limits for the metal/ligand bond dissociation activation energies rather than true thermodynamic binding energies. It could simply be that the $M^+(H_2O)_2$ and $M^+(NH_3)_2$ cluster ions dissociate at threshold at a much slower rate than monoligated ions and that a greater collision energy is required to achieve detectable dissociation on the time scale of the experiment (i.e., a "kinetic shift").[10] This is definitely ruled out, however, by the fact that we can obtain the correct H_2O and NH_3 binding energy order (i.e., second less than the first) for Na^+, K^+, H_3O^+, NH_4^+, F^-, and OH^- with our measurement technique. While some of the absolute solvent binding energies we obtain for these ions are slightly lower than the established literature values[1] (ca. 3–4

Table I. Water and Ammonia Binding Energies of Gas-Phase Ions[a]

M^+/n	1	2	3	4
	$D[M^+(H_2O)_{n-1}—OH_2]^b$			
V^+	35.1	35.5	12.2	
Cr^+	21.9	29.5		
Mn^+	26.5	17.8		
Fe^+	32.8	40.8		
Co^+	40.1	41.9		
Ni^+	39.7	40.6		
Cu^+			16.4^c	16.7^c
Ag^+	33.3^c	25.4^c	15.0^c	14.9^c
Na^+	21.0, 24.0^d	14.3, 19.8^d	15.8^d	13.8^d
K^+	15.2, 17.9^f	16.1^f	13.2^f	11.8^f
H_3O^+	30.7, 31.8^h	15.2, 19.0^h	17.6^h	11.5^h
NH_4^+	17.3^i	14.7^i	13.4^i	12.2^i
F^-	20.4, 23.3^j	16.6^j	13.7^j	13.5^j
OH^-	22.8, 26.8^h	17.6^h	16.2^h	12.2^h
	$D[M^+(NH_3)_{n-1}—NH_3]^b$			
V^+	51.9	45.0	22.6	18.7
Cr^+	37.4	40.8		
Mn^+	36.9	34.1	11.8	
Fe^+	38.5	48.7		
Co^+	58.8	61.1		
Ni^+	51.2	55.1	17.8	
Cu^+			14.0^c	12.8^c
Ag^+		36.9^c	14.6^c	13.0^c
Na^+	28.4, 29.1^e	17.0, 22.9^e	17.1^e	14.7^e
K^+	16.9, 20.1^g	16.3^g	13.5^g	11.6^g
NH_4^+	23.8, 24.8^i	15.7^i	13.8^i	12.5^i

[a] All values in kcal/mol. [b] This work unless otherwise noted. The precision for at least five measurements of each value is typically better than 0.1 eV (2 kcal/mol); the estimated uncertainty is better than ±0.2 eV (±4 kcal/mol). [c] Reference 8. [d] Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466. [e] Castleman, A. W., Jr.; Holland, P. M.; Lindsay, D. M.; Peterson, K. I. *J. Am. Chem. Soc.* **1978**, *100*, 6039. [f] Searles, S. K.; Kebarle, P. *Can. J. Chem.* **1969**, *47*, 2619. [g] Castleman, A. W., Jr. *Chem. Phys. Lett.* **1978**, *53*, 560. [h] Meot-Ner, M. *J. Am. Chem. Soc.* **1986**, *108*, 6189. [i] Payzant, J. D.; Cunningham, A. J.; Kebarle, P. *Can. J. Chem.* **1973**, *51*, 3242. [j] Arshadi, M.; Yamdagni, R.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1475.

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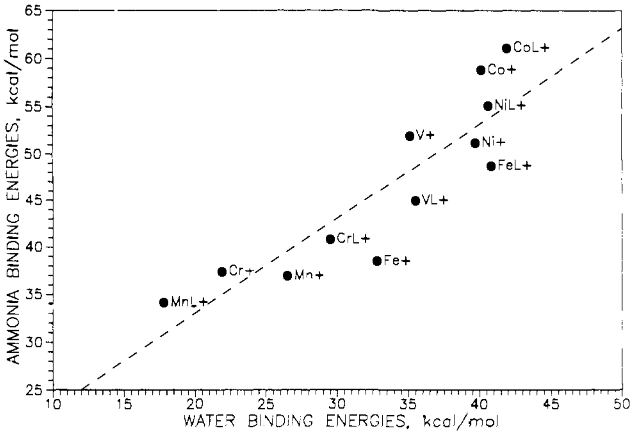

Figure 2. Comparison of water and ammonia binding energies for first-row transition-metal ion clusters. L is either H_2O or NH_3. The dashed line represents a best fit to the data (R = 0.88); slope = 1.00, intercept = 13.0 kcal/mol.

kcal/mol), the overall agreement is satisfactory.

Second, the cluster ions may not possess the presumed structures $M^+(H_2O)_n$ and $M^+(NH_3)_n$ but rather exist in metal-inserted forms: $H—M^+—OH$, $H—M^+—OH(H_2O)$ $(H)_2M^+(OH)_2$, $H—M^+—NH_2$, etc. Comparison of the available values for $D[M^+—OH]$, $D[M^+—NH_2]$, and $D[M^+—H]$ in the literature with the bond energies in H_2O and NH_3 suggests that such structures may be thermodynamically accessible.[11] Moreover, V^+ (but *not* the other metals) reacts with H_2O in the central quadrupole by dehydrogenation, and $V^+(H_2O)$ clusters undergo CID to produce $VO^+ + H_2$ in addition to $V^+ + H_2O$. Therefore, O—H insertion by V^+ must occur at some point during an ion-water collision or as a result of collisional activation of the stabilized adduct. We have investigated various ion/molecule reactions of the metal hydrate ions in search of chemical evidence for the presence of insertion structures, operating on the assumption that the $M^+—H$ moiety in such complexes should display characteristic reactivity. Perdeuterated metal hydrates $M^+(D_2O)_n$ formed in the flow reactor fail to undergo H/D exchange with H_2, $CH_2{=}CH_2$, or $CH_3CH{=}CH_2$ in the second quadrupole, whereas diatomic metal hydride ions MH^+ and metal hydride ion complexes readily exchange in the presence of D_2[12] and deuterated olefins.[13,14] Moreover, reactions between each of the $M^+(D_2O)_n$ cluster ions and H_2O in the second quadrupole proceed *exclusively* by water ligand substitution *without* H/D scrambling. Thus, the observed reactivity of the metal hydrates is inconsistent with insertion-type structures.[15]

$$M^+(D_2O)_n + H_2O \longrightarrow \begin{cases} \longrightarrow M^+(D_2O)_{n-1}(H_2O) + D_2O \\ \not\longrightarrow M^+(D_2O)_{n-1}(HOD) + HOD \end{cases}$$

The third and most likely origin of the unusual solvation energy orderings is the nature of the bonding between H_2O and NH_3 molecules and the transition-metal ions. Since purely electrostatic models cannot possibly account for the observed trends, then variations in the electronic configuration of the metal ions must play an important role.[16] Moreover, the visible aberrations in the correlation between the water and ammonia binding energies (Figure 2) suggest that the observed effects are a function of not only the metal but the ligand as well. In view of the many low-lying electronic states in atomic transition metal ions[17] and the likelihood of variable mixtures of s, p, and d bonding to H_2O and NH_3 ligands by the different metals,[18] large basis MCSCF calculations will undoubtedly be necessary to account for these unusual solvation energy trends.

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Registry No. V^{1+}, 14782-33-3; Cr^{1+}, 14067-03-9; Mn^{1+}, 14127-69-6; Fe^{1+}, 14067-02-8; Co^{1+}, 16610-75-6; Ni^{1+}, 14903-34-5; NH_3, 7664-41-7; H_2O, 7732-18-5.

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Highly Efficient Hydrolytic Cleavage of Adenosine Monophosphate Resulting in a Binuclear Co(III) Complex with a Novel Doubly Bidentate μ^4-Phosphato Bridge

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Cobalt complexes of the type *cis*-$[(N_4)Co(OH_2)_2]^{3+}$ where N_4 is any tetraamine ligand have been used extensively by various research teams as ATPase models and phosphatase models. Most of the model studies have been focused on phosphate anhydrides[1] (e.g., adenosine triphosphate (ATP)) or phosphate monoesters with good leaving groups[2] (e.g., *p*-nitrophenyl phosphate). Unactivated phosphate monoesters (e.g., adenosine monophosphate (AMP), methyl phosphate) are much more resistant to hydrolysis.[3] Here we report on a novel mechanism for efficient hydrolytic cleavage of unactivated phosphate monoesters leading to the formation of a binuclear cobalt(III) complex with a doubly bidentate phosphato bridge.

Stirring 2 equiv of $[(trpn)Co(OH_2)_2]^{3+}$ with disodium salts of adenosine monophosphate (AMP) or hydroxyethyl phosphate in water at 25 °C for about 6 h gave the corresponding alcohol and $[((trpn)Co)_2PO_4]^{3+}$ (**2**, Scheme I) in quantitative yield.[4] The

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