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Successive OH Binding Energies of $M(OH)_n^+$ for $n = 1-3$ and M = Sc, Ti, V, Co, Ni, and Cu

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The $M(OH)_n^+$ geometries, for $n = 1-3$, have been optimized and the zero-point energies computed using the B3LYP approach. The calculations show that strong bonds are formed for the early metals, and much weaker bonds are formed for the late metal atoms. The successive OH bond energies have been computed at the CCSD(T) level for $n = 1$ and 2. The M^+-OH bond energies are in good agreement with the guided ion beam results. This implies that the CID values for $TiOH^+$, VOH^+, and $CoOH^+$, and the photodissociation value for $CoOH^+$ are accurate, but that the CID values for $ScOH^+$ and $NiOH^+$ are too small. The B3LYP binding energies are found to be in qualitative agreement with the CCSD(T) results. The relative size of the first and second OH binding energies at the B3LYP level disagrees with the CCSD(T) for Sc^+, Ti^+, and V^+. The B3LYP results show that the third OH binding energy for Ti^+ and V^+ will be large (85 kcal/mol, or more), while for the remaining systems the third OH is electrostatically bound, with a binding energy of only about 30 kcal/mol.

1. Introduction

We recently studied[1] $Sc(OH)_n^+$, for $n = 1-3$. While this study was motivated by the experiments by Crellin et al.,[2] the computational study showed that the metal−ligand (M−L) bonding in $Sc(OH)_n^+$ was very interesting. $ScOH^+$ was a linear system, while $Sc(OH)_2^+$ had an OScO angle of 120° and an ScOH angle of 162°. The nonlinear ScOH subunit suggests that the second Sc−OH bond is less ionic than the first. However, the second OH was shown to be more strongly bound than the first. With only two valence electrons, the third OH was much less strongly bound than the first two OH molecules. That is, there were interesting changes in the bonding, bond energies, and geometries with number of ligands. In addition, we found that density functional theory (DFT) showed some interesting differences from the more accurate coupled cluster approach, so these systems are also interesting from a computational point of view. In this work, we consider the same ligand with several additional metal atoms, two from the left side and three from the right side of the first transition row. We note that the MOH^+ systems have been studied in experiment,[3−8] and therefore the experiments on the single OH systems help to calibrate the computational study.

2. Methods

The geometries are optimized and vibrational frequencies computed using DFT in conjunction with the B3LYP[9] hybrid[10] functional. The computed frequencies confirm that these structures correspond to minima, and they are used to compute the zero-point energies. We should note that we obtained several local minima for these systems, especially for $M(OH)_3^+$. To minimize the possibility that we have not found the global minima, the geometry optimizations were started from several different initial geometries, including the optimal structures of the other $M(OH)_n^+$ systems and structures that were not the minimum for any of the systems considered.

Using the B3LYP geometries, the OH binding energies are also computed using the coupled cluster singles and doubles approach[11] including the effect of unlinked triples, which is determined using perturbation theory;[12] this approach is denoted CCSD(T). The restricted open-shell CCSD(T) approach[13,14] is used. In the CCSD(T) calculations, the O 1s-like orbitals are not correlated. For the metal atoms, the 1s-like to 2p-like orbitals are not correlated for Sc to V, while for Co to Cu the 1s-like to 3p-like orbitals are not correlated.

In the DFT calculations, the metal basis sets are a [8s4p3d] contraction of the (14s9p5d) primitive set developed by Wachters.[15] The s and p spaces are contracted using contraction number 3, while the d space is contracted (311). To these basis sets, two diffuse p functions are added; these are the functions optimized by Wachters multiplied by 1.5. A diffuse d function[16] is also added. The O and H basis sets are Dunning's double-ζ contraction[17] of the Huzinaga primitive sets.[18] To the oxygen, a diffuse sp set with an exponent of 0.0845 and a 3d polarization function with an exponent of 0.85 are added. The hydrogen set is scaled by 1.2, and a 2p polarization function, with an exponent of 1.0, is added.

In the CCSD(T) calculations, the O and H basis sets are the augmented correlation-consistent polarized-valence triple-ζ (aug-cc-pVTZ) sets developed by Dunning and co-workers.[19,20] The metal basis sets are derived from the averaged atomic natural orbital[21,22] (AANO) set described in ref 23. For Co to Cu they are used without modification, while for Sc to V they are modified to allow 3s and 3p correlation. For Sc and Ti, the first 17 s functions are contracted to three functions using the AANO orbitals, while the four most diffuse s primitives are uncontracted. The first 10 p functions are contracted to two functions, while the six most diffuse primitives are uncontracted. Because V has one less primitive s and one less primitive p, only the first 16 s and nine p functions are included in the contraction. The four d AANOs are supplemented by uncontracting two d functions in the region of the 3p orbital, namely those with exponents of 1.342 621 and 0.561 524 for Sc, 1.689 268 9 and 0.715 670 6 for Ti, and 1.482 482 and 0.661 351 0 for V. The unmodified three f and two g polarization sets are used. Thus the final Sc and Ti basis set are of the form (21s16p9d6f4g)/[7s8p6d3f2g]. For V, this yields a basis set of the form (20s15p10d6f4g)/[7s8p6d3f2g].

The CCSD(T) calculations were performed using MOLPRO

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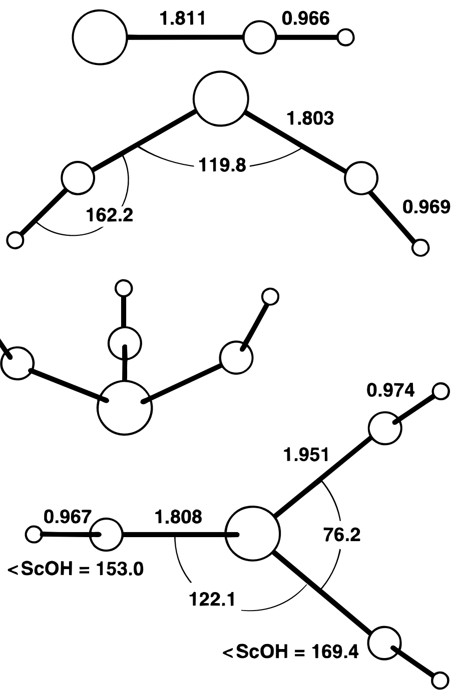

Figure 1. B3LYP structures of Sc(OH)$_n^+$, for $n = 1-3$; taken from ref 1. The bond lengths are in angstroms and the bond angles in degrees. For comparison the bond length of free OH at this level of theory is 0.982 Å.

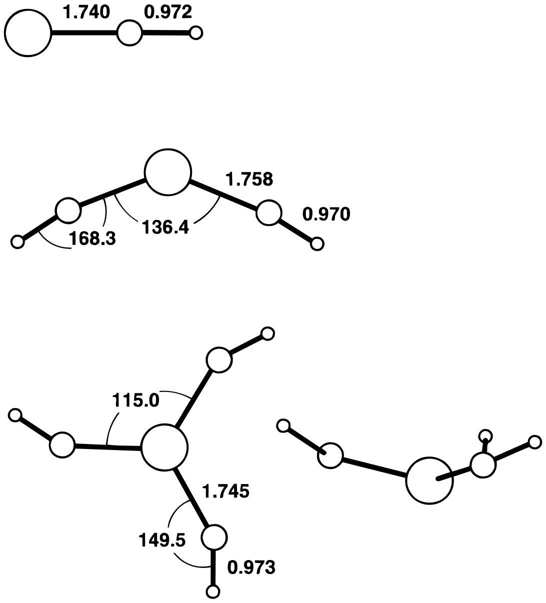

Figure 2. B3LYP structures of Ti(OH)$_n^+$, for $n = 1-3$. The bond lengths are in angstroms and the bond angles in degrees.

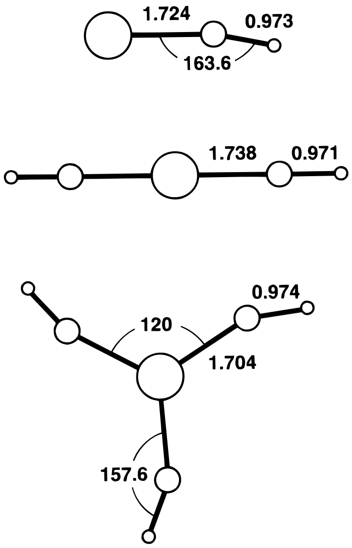

Figure 3. B3LYP structures of V(OH)$_n^+$, for $n = 1-3$. The bond lengths are in angstroms and the bond angles in degrees. V(OH)$_2^+$ is linear, and V(OH)$_3^+$ is planar.

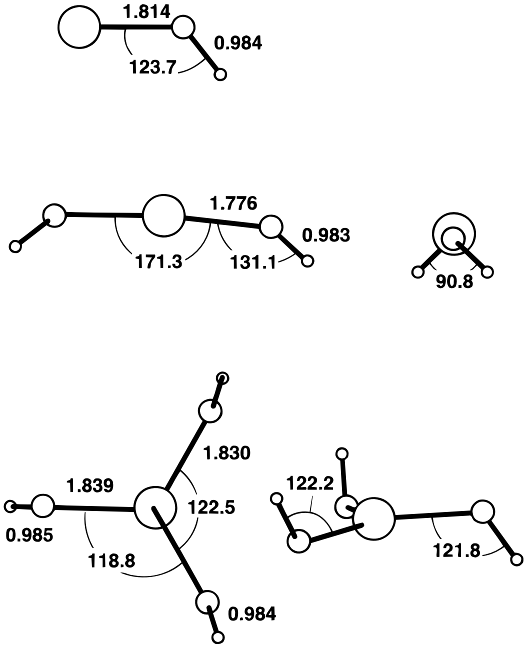

Figure 4. B3LYP structures of Cu(OH)$_n^+$, for $n = 1-3$. The bond lengths are in angstroms and the bond angles in degrees.

96.[24] The B3LYP calculations were performed using Gaussian 94.[25] Only the spherical harmonic components of the basis sets were used.

3. Results and Discussion

3.1. Geometry and Bonding. The optimal B3LYP geometries are shown in Figures 1−6. For completeness, we start with Sc(OH)$_n^+$ even though these systems have been discussed previously.[1] ScOH$^+$ is linear (see Figure 1), with a $^2\Delta$ ground state. The bonding is derived mostly from Sc$^+$ ^{3}F(3d^2) with a 3d$\pi^1$3dδ^1 occupation. This occupation allows a bond between the 3dπ and OH 1π orbitals as well as donation from the OH doubly occupied 1π and 3σ orbitals into empty Sc$^+$ orbitals. The Sc 3dπ−OH 1π bond is polarized toward the OH, giving the bond significant ionic character. The net Sc charge is 1.47, showing that the charge polarization in the bond is larger that the donation of the doubly occupied OH orbitals to Sc. Sc(OH)$_2^+$ is a singlet with two Sc−OH bonds. With two OH molecules, the OScO is bent to allow the OH molecules to donate into different 3d orbitals as well as allow for any covalent bonding that arises from Sc sd hybridization. Since the Sc donation per ligand is reduced with increasing numbers of ligand, the bonding becomes less ionic and more covalent for Sc(OH)$_2^+$ than for ScOH$^+$. This change in Sc to OH donation is observed in the net Sc charge, which is 1.81 or 0.41 electrons per OH for Sc(OH)$_2^+$ compared with the value of 1.47 for ScOH$^+$. The bending of the ScOH subunits in Sc(OH)$_2^+$ reflects the reduced ionic and increased covalent bonding. With only two valence electrons on Sc$^+$, the third OH is electrostatically bound and the molecule is a doublet, as expected. The change in bonding with the addition of the third OH is clearly

TABLE 1: Computed D_0 Values (in kcal/mol). The B3LYP Geometries and Zero-Point Energies (ZPE) Are Used Throughout

	CCSD(T)	B3LYP	best	expt
Sc^+-OH doublet	117.5	118.8	120.5 ± 3	119.2 ± 2.1[a], 87.8 ± 3[b]
$ScOH^+-OH$ singlet	124.1	117.7	127.1 ± 3	
$Sc(OH)_2^+-OH$ doublet		32.4		
Ti^+-OH triplet	108.9	116.3	111.9 ± 3	111.2 ± 2.8[a], 113.0 ± 3[b]
$TiOH^+-OH$ doublet	114.9	109.7	117.9 ± 3	
$Ti(OH)_2^+-OH$ singlet		96.5		
V^+-OH quartet	95.6[c]	96.1	98.6 ± 3	101.7 ± 4.4[d], 103.8 ± 3.5[a], 107.0 ± 3[b]
VOH^+-OH triplet	97.6	95.2	100.6 ± 3	
$V(OH)_2^+-OH$ doublet		85.3		
Co^+-OH quartet	65.1	66.8	68.1 ± 3	71.7 ± 0.9[e], 72.2 ± 3[b], 71 ± 3[f]
$CoOH^+-OH$ quintet	60.6	65.9	63.6 ± 3	
$Co(OH)_2^+-OH$ sextet		34.3		
Ni^+-OH triplet	50.7	59.7	53.7 ± 3	56.3 ± 4.6[g], 42.2 ± 3[b]
$NiOH^+-OH$ quartet	41.0	52.3	44.0 ± 3	
$Ni(OH)_2^+-OH$ quintet		31.8		
Cu^+-OH doublet	28.4	38.7	30.4 ± 2	
$CuOH^+-OH$ triplet	34.0	44.3	36.0 ± 2	
$Cu(OH)_2^+-OH$ quartet		27.3		

[a] Reference 4, for OD at 0 K, using guided ion beam. [b] Reference 3, using CID; the temperature is not well defined. [c] The B3LYP linear geometry is used. [d] Reference 5, for OD at 0 K, using guided ion beam. [e] Reference 6, at 0 K, using guided ion beam. [f] Reference 8, at 298 K, using photodissociation. [g] Reference 7, at 0 K, using guided ion beam.

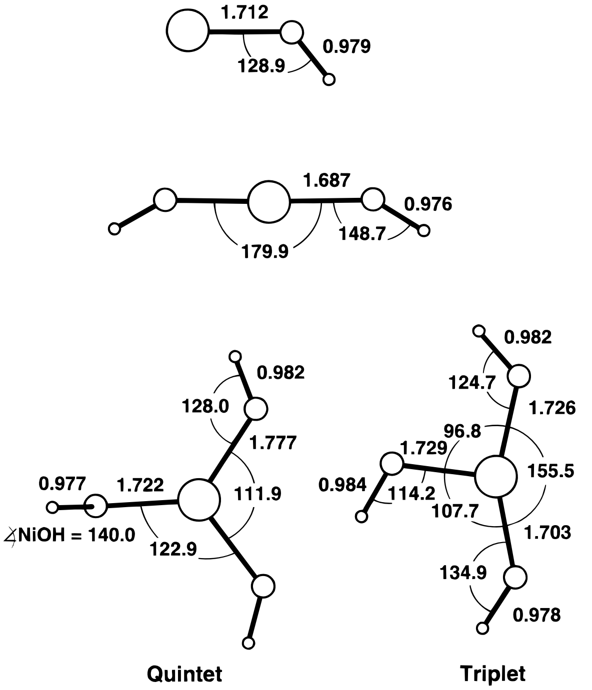

Figure 5. B3LYP structures of $Ni(OH)_n^+$, for $n = 1-3$. The bond lengths are in angstroms and the bond angles in degrees. $Ni(OH)_2^+$ is planar, and $Ni(OH)_3^+$ triplet is only slightly distorted from planar.

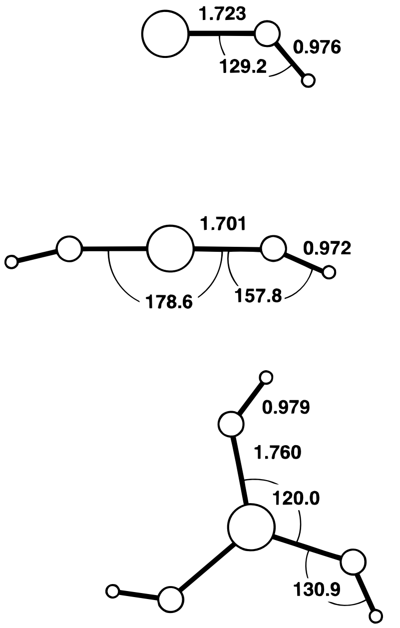

Figure 6. B3LYP structures of $Co(OH)_n^+$, for $n = 1-3$. The bond lengths are in angstroms and the bond angles in degrees. All of the systems are planar.

observed in the dramatic decrease in the third binding energy; see Table 1. One might expect $Sc(OH)_3^+$ to look like one OH weakly bound to a slightly perturbed $Sc(OH)_2^+$. Instead we find one Sc−OH bond with a short Sc−O distance and two long Sc−OH bonds, sharing one Sc valence electron; see Figure 1.

$TiOH^+$ is a linear triplet as expected; see Figure 2. One metal 3dπ−OH 1π bond is formed, as for $ScOH^+$. The other 3dπ orbital is empty to maximize OH π donation to the metal. The $3d\delta^2$ occupation would minimize the Ti−OH repulsion and maximize the OH to Ti donation; however, $3d\pi^1 3d\delta^2$ is 40% ground-state ^4F and 60% ^4P, which is more than 20 kcal/mol above ^4F, and hence the bonding is derived from $3d\sigma^1 3d\pi^1 3d\delta$,[1] which is 100% ^4F. This results in a $^3\Delta$ ground state, with the $^3\Sigma^-$ state being 4.8 kcal/mol higher in energy. In the $^3\Delta$ state, the σ repulsion is reduced by sdσ hybridization. The net Ti charge in the ground state is 1.38. This is smaller than for $ScOH^+$, which is consistent with the increased ionization potential of Ti^+ compared with Sc^+. There are two metal−OH bonds in $Ti(OH)_2^+$, and not surprisingly the structure of the $^2A_1$ ground state of $Ti(OH)_2^+$ is similar to that of $Sc(OH)_2^+$, although the OMO angle is larger for Ti than Sc. The net Ti charge is 1.68, which shows a donation of 0.34 electrons to each OH molecule, which is slightly smaller than found for $TiOH^+$. The structure of $Ti(OH)_3^+$ is completely different from $Sc(OH)_3^+$, since with three valence electrons, Ti can form three strong metal−OH bonds; note that the Ti−O bond lengths are similar for all three systems. $Ti(OH)_3^+$ is slightly nonplanar, and the M−OH angle is even smaller than for $Ti(OH)_2^+$ as the metal to OH donation, 0.25 electron to each OH, is still smaller than for $TiOH^+$ and $Ti(OH)_2^+$.

VOH^+ is slightly bent at the B3LYP level; see Figure 3. For a linear geometry, there are clearly two low-lying states, the $^4\Sigma^-$ state derived from $3d\sigma^1 3d\pi^1 3d\delta^2$ and the $^4\Pi$ state derived from $3d\pi^2 3d\delta^2$. In both a bond is formed between the V 3dπ and OH 1π orbitals. The $^4\Sigma^-$ state allows better OH π donation, while the $^4\Pi$ state allows better OH σ donation. Bending allows these states to mix, and at the B3LYP level, this mixing leads to a bent molecule. However, the energy lowering associated with this bending is only 0.05 kcal/mol. At the CCSD(T) level, the linear structure is 1.46 kcal/mol below the bent; thus we suspect that VOH^+ is actually linear.

$V(OH)_2^+$ is linear with a $^3\Sigma_g^-$ ground state that is derived from the V^+ $3d\pi^2 3d\delta^2$ occupation. This allows each OH to form a bond with a V 3dπ orbital and minimizes the V−OH σ repulsion. As more nonbonding d electrons are added from Sc to V, the OMO angle increases, until for $V(OH)_2^+$ only the 3dσ orbital is empty and the OH molecules must be on opposite sides of the metal to allow OH σ donation to the empty 3dσ orbital. The VOH subunits remain linear since bending the VOH without bending OVO increases the metal−OH repulsion.

$V(OH)_3^+$ looks similar to $Ti(OH)_3^+$, and like $Ti(OH)_n^+$ the V−O bond distances vary only slightly with number of ligands. In addition, the V−OH bond energies show a relatively small change with the number of ligands. That is, with four valence electrons, the bonding in the $V(OH)_n^+$ systems is similar for one, two, or three OH ligands. Assume $V(OH)_3^+$ is in the xy plane. Then relative to $Ti(OH)_3^+$, the extra, nonbonding, electron is in the out-of-plane 3dσ orbital, which results in $V(OH)_3^+$ being planar.

We now consider three systems from the right side of the first transition row. We start with Cu^+, which has a closed-shell $3d^{10}$ occupation, and the bonding is the simplest. The optimal structures are shown in Figure 4. $CuOH^+$ is bent with a $^2A'$ ground state, with the linear configuration being 3.8 kcal/mol higher at the B3LYP level. The bonding is mostly electrostatic. The charge−dipole contribution to the bonding favors a linear molecule, but bending allows the open-shell OH 1π orbital to donate to the Cu^+ 4s orbital. This dative interaction, plus some 4s−1π covalent bonding arising from $3d^{10}$ to $3d^9 4s^1$ promotion, results in a bent molecule. The Cu promotion is clearly visible in the Cu 3d population of 9.70 electrons. As expected most of the open-shell character is on the OH. The net Cu charge is 0.82, indicating that OH to metal donation is larger than metal to OH donation. This is opposite to what is found for the metal atoms on the left side of the row. $Cu(OH)_2^+$ is a nearly linear molecule with bonding similar to that in $CuOH^+$. The electrostatic bonding results in a triplet state. The OH molecules are on the opposite sides of the Cu, as this minimizes the OH−OH repulsion. The CuOH subunits are not in the same plane, as this also reduces the OH−OH repulsion. The Cu−OH repulsion is reduced by sdσ hybridization, which reduces the electron density on both sides of the Cu. This results in a contraction of the Cu−O bond when the second OH is added. Since the two ligands share the cost of the hybridization, the second ligand is more strongly bound than the first; see Table 1. The singlet state derived by forming two Cu−OH bonds from the Cu^+ $^3D(3d^9 4s^1)$ state is much higher in energy, which is consistent with the large promotion energy[26] for Cu^+. The sdσ hybridization is not efficient at reducing the metal−ligand repulsion for three ligands, and hence the third OH is less strongly bound than the first two. The $Cu(OH)_3^+$ structure is the one that minimizes the OH−OH repulsion. Note that the structure with all three H atoms on the same side of the plane containing the O atoms is only 0.8 kcal/mol higher than the one shown in Figure 4. The doublet state with two Cu−OH bonds is significantly above the quartet ground state with electrostatic bonding. Clearly the bonding in $Cu(OH)_n^+$ is very different from the metals on the left side of the first transition row.

Ni and Co have open-shell electrons such as the metals on the left side of the row, but Ni and Co do not have empty 3d orbitals. Rather than empty 3d orbitals, Ni and Co have doubly occupied orbitals such as Cu. Thus the interesting question is, are Ni and Co like Sc, Ti, and V, or like Cu, or, perhaps, completely different from these two cases. We first consider $Ni(OH)_n^+$. Ni^+ has a $^2D(3d^9)$ ground state, with the $^4F(3d^8 4s^1)$ state 25.0 kcal/mol higher in energy.[26] For $NiOH^+$ several bonding mechanisms are possible; one possibility is the formation of a Ni−OH bond, as found for the metals on the left side. This would yield a singlet state for the $3d^9$ occupation and a triplet state if the bonding were derived from the $3d^8 4s^1$ occupation. This bond could range from covalent to ionic in character. Electrostatic bonding is another possibility, where the open shell on OH is high spin coupled to the Ni open shells. This would produce a triplet state for the $3d^9$ occupation and a quintet state for the $3d^8 4s^1$ occupation.

At the B3LYP level, the ground state is found to be a triplet state, with the singlet 38.3 kcal/mol higher in energy. The separation is 33.8 kcal/mol at the CCSD level, but 12.5 kcal/mol at the CCSD(T) level. Unfortunately the norm of the singles amplitudes is large for the singlet state. Therefore it is difficult to accurately determine the separation between the states, but it is clear that the ground state is a triplet with a bent geometry, see Figure 5. (Note that the bent structure is below the linear at both the CCSD(T) and B3LYP levels of theory.) Unlike the metals on the left side of the row, forming a chemical bond between the open 3d orbital in the Ni $3d^9$ occupation and OH 1π is unfavorable. We suspect that the repulsion between the doubly occupied 3d orbitals and the occupied OH 3σ and 1π orbitals results in significant Ni−OH repulsion at the bond length optimal for chemical bonding. That is, on the right side there is metal repulsion, while on the left there is bonding from the OH donation to empty orbitals.

The bonding in the triplet state is quite complex and appears to be derived from a mixture of $3d^9$ and $3d^8 4s^1$; the 3d population is 8.55 electrons. This mixing of asymptotes can occur only for the triplet state and is probably the reason that it is the ground state. In the triplet state, the open-shell population on OH is 0.54 electrons, which is consistent with half a bond between Ni and OH. The net charge on Ni is 1.00, showing that the Ni to OH and OH to Ni donations cancel. One way to view the bonding in $NiOH^+$ is to start from $3d^9$ with the 3dσ singly occupied to minimize the Ni−OH repulsion; then 3dπ electrons are donated to the open-shell OH π orbital, thus increasing the open-shell character on Ni and decreasing it on the OH. The alternative is to start from Ni^+ $3d^8 4s^1$, and form a covalent bond between the 4s+3dσ hybrid and OH π orbital. The out-of-plane doubly occupied OH π orbital donates electrons into the singly occupied 3dπ orbital, thus creating open-shell character on OH. The Mulliken populations and orbitals show the bonding is a complex mixture of these two extremes.

The bonding in $Ni(OH)_2^+$ is very similar to that in $NiOH^+$. The ground state is a quartet that is a mixture of chemical bonding from $3d^8 4s^1$ and electrostatic bonding from 3d.[9] It can be viewed as high-spin coupling an OH to the ground state of $NiOH^+$. The sdσ hybridization and singly occupied 3dσ character are responsible for the essentially linear ONiO subunit. The open-shell character on each OH is 0.61 electron, which is slightly larger than the 0.54 electron for $NiOH^+$. The slight reduction in the metal to OH donation is due to the increased total charge on Ni for two OH molecules. With two OH molecules to donate to Ni and a reduction in the Ni donation to an individual OH, it is not surprising to find a net charge on Ni of 0.81 electron. Even though there are two OH molecules sharing the cost of sdσ hybridization, which reduces the Ni$-$3σ repulsion, the second OH is less strongly bound than the first. Apparently the reduction in the bonding due to the smaller Ni to OH donation is larger than any gain due to sharing the cost of the sdσ hybridization. The doublet state, with more chemical bonding, is 9.7(1.2) kcal/mol higher at the B3LYP-(CCSD(T)) level. This is a significant drop from $NiOH^+$. This is probably a result of the two ligands sharing the cost of the promotion energy to $3d^84s^1$ and sharing the loss of Ni exchange energy when the bond is formed.

For $Ni(OH)_3^+$ at the B3LYP level, the quintet and triplet states are essentially degenerate; the triplet is lower without zero-point energy, and the quintet is lower with zero-point energy. Even the singlet state, which involves three Ni$-$OH bonds like those for the metals on the left side of the row, is only 5.8 kcal/mol higher. For the quintet state the open-shell character on each OH is 0.80 electron, which shows that $Ni(OH)_3^+$ has significantly more electrostatic bonding and less chemical bonding than $NiOH^+$ or $Ni(OH)_2^+$. The net charge on Ni is 0.63 electron, showing a growing importance of OH to Ni donation relative to Ni to OH donation as the number of ligands increases. Thus as the number of OH molecules increases, the low-spin states with Ni$-$OH chemical bonding become more competitive with respect to the high-spin states with electrostatic bonding. Given the accuracy of the B3LYP approach, we are unable to definitively determine the ground state of $Ni(OH)_3^+$; however, it is clear that the third ligand bond energy is significantly smaller than the first two. Thus the difference in OH bond energies for Ni and Cu decreases from about 20 kcal for the first OH to 4 kcal/mol for the third OH.

We should note that the determination of the ground-state $Ni(OH)_3^+$ is complicated by many minima on the potential energy surfaces, which differ mostly in the orientation of the OH molecules and orientation of the open-shell 3d orbitals. For example, the triplet state, formed by rotating one OH by 180° so that it is still planar but with all H atoms pointing in a clockwise direction, is only 3.1 kcal/mol above the lowest triplet shown in the figure. Rotating the OH molecules so that all H atoms point in the same direction out of the plane of the Ni and oxygen atoms is also a minimum on the potential energy surface and is 12 kcal/mol above the lowest triplet.

The bonding in $Co(OH)_n^+$ is very similar to that in $Ni(OH)_n^+$, except with one more open-shell 3d orbital, the multiplicity of the $Co(OH)_n^+$ systems is one larger than for the analogous $Ni(OH)_n^+$ systems. The structures of $CoOH^+$ and $Co(OH)_2^+$ are clearly similar to those found for Ni systems; compare Figure 5 and Figure 6. $Co(OH)_3^+$ is a planar sextet state, while the quintet state of $Ni(OH)_3^+$ has one OH rotated out of the plane. The additional open shell in Co appears to cause small changes in the relative separation of the different minima; for example the planar quintet state of $Ni(OH)_3^+$, which is analogous to the sextet state of $Co(OH)_3^+$, is 1 kcal/mol (0.7 kcal/mol with zero-point energy) above the one shown in Figure 5. The additional exchange energy associated with the extra open shell in Co results in the quartet state being 2.7 kcal/mol above the sextet, whereas the triplet and quintet states are essentially degenerate for $Ni(OH)_3^+$. However, these differences between $Co(OH)_n^+$ and $Ni(OH)_n^+$ are small when compared with the differences between them and those on the left side of the first transition row or between them and $Cu(OH)_n^+$.

3.2. OH Bond Energies. The OH bond energies are summarized in Table 1. Our best results are those computed using the CCSD(T) approach; however, even these values need to be corrected for limitations in the theory. It has been observed[27] that the CCSD(T) approach is usually reliable if the norm of the singles amplitudes divided by the square root of the number of electrons correlated is smaller than 0.03. The values for most of the systems reported in Table 1 are smaller than this guideline and only slightly larger in the worst cases. For example, of the systems with one OH, $NiOH^+$ has the large norm (0.148), while $CoOH^+$ has the second largest value (0.077). For the systems with two OH molecules, Co and Ni again have the largest values of 0.174 and 0.140, respectively. Considering the small values for the norm of the singles and large basis set used, the CCSD(T) results are expected to have a maximum error of about 3 kcal/mol for all systems except $Cu(OH)_n^+$, where we suspect that the mostly electrostatic bonding should be easier to describe, and hence the maximum error should be about 2 kcal/mol. Excluding $Cu(OH)_n^+$, we make our best estimate by adding 3 kcal/mol to the computed CCSD(T) value and assigning an error bar of ±3 kcal/mol. For $Cu(OH)_n^+$ we add 2 kcal/mol and assign an error bar of ±2 kcal/mol.

For those systems with Sc, Ti, V, and Cu, the CCSD(T) calculations were straightforward; this was not the case for $Co(OH)_n^+$ and $Ni(OH)_n^+$. For these systems there were two or more states very close in energy at the HF level. For example in $NiOH^+$, there were two $^3A''$ states that arose from the two ways to put three electrons in the two 3d orbitals in the a'' symmetry; these two states differ by only 0.2 kcal/mol. The higher of the two states has the same open-shell 3d orbital as in the B3LYP calculation. Since the orbitals are very different for these two states, it is possible to perform CCSD(T) calculations for both of them. With the addition of electron correlation, the order of the two states reverses; at the CCSD and CCSD(T) levels the separations are 3.7 and 4.9 kcal/mol, respectively. Thus, in addition to being useful in the determination of the equilibrium geometry, the B3LYP calculations can help ensure that the ground state has been correctly found in the HF calculations. While there are several low-lying states for $CoOH^+$ and $Co(OH)_2^+$, it is encouraging that the HF solution yielding the lowest CCSD(T) energy is the one that is the most similar to the B3LYP result.

$Ni(OH)_2^+$ is the most extreme example of the problem with multiple HF solutions, where we find four solutions within 2.5 kcal/mol, with the lowest two differing by only 0.35 kcal/mol. The HF solution with the third highest energy has the open-shell orbitals localized on the Ni and produces a norm of the singles amplitudes of 0.55 in the CCSD calculation. That is, the CCSD approach fails since the reference wave function is missing the very important mixing of the 3d and OH π orbitals. The other three HF solutions are much more similar to the B3LYP, showing mixing of the Ni 3d and OH 1π in the open-shell orbitals. Unfortunately none of the solutions look exactly like the B3LYP solution, and therefore CCSD(T) calculations where performed for all three. The second and fourth roots yield CCSD(T) energies that differ by 0.1 kcal/mol, while the lowest HF solution yields a CCSD(T) energy that is 12.6 kcal/mol higher in energy. While none of these three HF solutions look exactly like the B3LYP, we believe that the second and fourth roots are sufficiently similar to the B3LYP solution that one of these nearly degenerate state is the ground state of $Ni(OH)_2^+$ at the CCSD(T) level.

We compare our computed values with experiment in Table 1. We should note that several of the experiments are for MOD^+ and many are at 298 K. For $ScOH^+$ we considered these effects, and substituting OD for OH increases the OH binding energy by 0.4 kcal/mol; the value at 298 K is 1.3 kcal/mol larger than at 0 K. For $ScOH^+$ our best estimate for the $Sc^+$$-$OH binding energy is in good agreement with the guided ion beam value for $ScOD^+$ by Armentrout and co-workers,[4] but is much larger than the value of Michl and co-workers[3] determined using collision-induced dissociation (CID). In the CID experiments, the temperature is not well established and the clusters could be thermally and electronically excited, which could be responsible for the small value. For $TiOH^+$, our best estimate is in very good agreement with both the guided ion beam and CID results. For VOH^+, our best estimate overlaps with the guided ion beam results and is slightly smaller than the CID value. We feel that the theory shows that the true result is in the lower ranges of the experimental results. For $CoOH^+$, the theoretical and experimental values overlap, again suggesting that the true value lies in the lower part of the experimental range and the upper part of the best estimate based on theory. $NiOH^+$ is like $ScOH^+$; our best estimate agrees with the guided ion beam result to within their mutual error bars, but our value is significantly larger than the CID result. Since our CCSD(T) value cannot be 8 kcal/mol too large, the CID result must be significantly too small. As for $ScOH^+$, the small CID value could be a result of excited states in experiment.

Given the good agreement between theory and the guided ion beam experiments for $ScOH^+$, $TiOH^+$, VOH^+, $CoOH^+$, and $NiOH^+$, we are confident that our other values are also accurate to within their estimated uncertainties. The only possible exception is $Ni(OH)_2{}^+$, where the HF solution was not as similar to the B3LYP as found for the other systems. Since we were unable to find a better solution, we are cautiously optimistic that this result is also correct.

The B3LYP and CCSD(T) values or B3LYP and our best estimates are only in qualitative agreement. It is especially disappointing that the B3LYP binding energy for $Cu^+{-}OH$ is 8 kcal/mol larger than our best estimate, because the bonding in this system is relatively easy to describe. The overbinding appears[28] to be common for open-shell ligands, while for closed-shell ligands the B3LYP and CCSD(T) approaches appear to be in much better agreement.[29,30] The errors in the B3LYP approach do not appear to arise from the small basis set used. This possibility was tested by computing the $Sc^+{-}OH$ and $Ni^+{-}OH$ B3LYP binding energies using the much larger 6-311+G(2df,2p) basis[25,31,32] (at the smaller basis B3LYP geometries). Using this larger basis set decreased the $Sc^+{-}OH$ and $Ni^+{-}OH$ binding energies by 0.8 and 0.4 kcal/mol, respectively.

The trends in the first two OH binding energies at the B3LYP level show some correlation with the CCSD(T) values. The second OH is clearly less bound than the first for Ni^+ and more strongly bound than the first for Cu^+, and the first and second OH binding energies are very similar for V^+. However for the other three systems, the B3LYP and CCSD(T) differ. For Sc^+ and Ti^+, the CCSD(T) shows that the second is more strongly bound than the first, whereas the B3LYP has the first more strongly bound than the second. For $ScOH^+$ and $TiOH^+$, the bonding is derived from d^{n+1}, but the atomic ground state is derived from $3d^n4s^1$. The B3LYP approach, and DFT in general, favors the d^{n+1} occupation. Thus if the binding energy is computed with respect to the $3d^n4s^1$ occupation, the binding energy is too large. This error does not occur for the second and third bond energies, since the 3d occupation of the metal atoms does not change significantly. If the first OH binding energy is computed with respect to the $3d^{n+1}$ asymptote and corrected to the ground state using experiment,[26] the values for $Sc^+{-}OH$ and $Ti^+{-}OH$ are reduced by 8.8 and 7.5 kcal/mol, respectively. This correction improves the agreement of the $TiOH^+$ B3LYP binding energy with the CCSD(T) result and degrades the agreement for $ScOH^+$, but it improves the agreement for the change in binding energy with number of OH molecules for both Sc^+ and Ti^+. However this correction is not quantitative; for Ti^+ the corrected B3LYP results show the second OH is 0.9 kcal/mol more strongly bound that the first, which is significantly smaller than the 6 kcal/mol found at the CCSD(T) level. The ground state of Co^+ is derived from the d^8 occupation, and therefore the B3LYP would underestimate the contribution from $3d^74s^1$ in the $CoOH^+$ bonding. This should result in a binding energy that is too small. Thus correcting $CoOH^+$ for the limitations of the B3LYP approach would increase the first OH bond energy, making the agreement with the CCSD(T) worse, but would improve the difference between the first and second OH binding energies. While the B3LYP errors in the atomic separations give us some insight into the difference between the CCSD(T) and B3LYP molecular binding energies, it is difficult to design an accurate correction for the B3LYP approach. Thus it is only safe to use the B3LYP for trends after some calibration has been performed.

While the B3LYP approach cannot be trusted for small differences in OH binding energies with number of ligands, the differences for the third OH are so large that the B3LYP offers some insight into the trends, especially when it is realized that the metal 3d populations are not changing significantly so that the difference between the second and third OH binding energies is expected to be more accurate than the difference between the first and second. For Sc^+ there is clearly a large drop due to Sc^+ having only two valence electrons. The third OH binding energies for Ti^+ and V^+ are clearly close to the first two; the approximately 10 kcal/mol drop in the third binding energy is probably due to increased OH−OH repulsion. The third OH is clearly much less strongly bound than the first two for Co^+ and Ni^+. The value for the third OH is close to that for Cu^+, and this suggests that for three OH molecules the bonding has become mostly electrostatic for Co^+ and Ni^+.

$Cu(OH)_3{}^+$ is a special case since the Cu undergoes small changes with number of OH molecules, and therefore the trends in the B3LYP binding energies are expected to be the most accurate. As note above, sharing the cost of sdσ hybridization results in the second OH being more strongly bound than the first. However, it is not possible to arrange three OH molecules so that all can benefit from the reduced Cu−OH repulsion, and hence the sdσ hybridization is lost and the third OH is the least strongly bound. This has been discussed[33] in detail for $Cu(H_2O)_n{}^+$, and the B3LYP results for $Cu(OH)_n{}^+$ are consistent with the expected trend.

4. Conclusions

The CCSD(T) binding energies for $M^+{-}OH$ are in good agreement with the guided ion beam experiments. The CID values for $Sc^+{-}OH$ and $Ni^+{-}OH$ are clearly too small, while the other CID values appear reasonably accurate. The photodissociation experiment for $CoOH^+$ is in good agreement with our best estimate. The B3LYP binding energies are in qualitative agreement with the CCSD(T) results. Apparently the B3LYP approach does not work as well for open-shell ligands as for closed-shell ones. Despite the limitations in the binding energies, the B3LYP approach does appear to be a good method of optimizing the geometry and helping to determine the ground state. The B3LYP also offers some insight into the trends in binding energies, but caution must be shown in interpreting energy differences of less than 10 kcal/mol.

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