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Metal Cation Binding to Phenol: DFT Comparison of the Competing Sites

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The two metal ion binding regions of phenol were characterized and compared by density functional theory (DFT). The monocations of sodium, magnesium, aluminum, and the first-row transition series were considered, using mainly the B3LYP and MPW1PW91 functionals. Calculations on the model ligands water and benzene were carried out at the same level of theory. The MPW1PW91 functional is more favorable than the B3LYP functional toward binding to the aromatic ring, while no strong difference is seen for oxygen binding. Comparison with experimental data and higher level computational results for water and benzene indicate that MPW1PW91 is better than B3LYP in predicting the differential between ring and oxygen binding energies, and seems to do an excellent job of making this comparison. Except for Na^+, for which the ring and oxygen neighborhoods have similar binding energies, the ring site of phenol was favored for all the metal ions. The differential was quite small (2−3 kcal mol^{-1}) for Mg^+, for which the O site may have significant thermal population at ordinary temperatures. Al^+, Cr^+, and Mn^+ showed ring/O differential binding energies of 5−6 kcal mol^{-1}, which probably rules out significant thermal populations of the oxygen site. The other transition metal ions all showed very large ring/O binding energy differentials. The ring/O binding differentials for phenol were accurately mirrored by the differentials between binding of the same metal ions to benzene versus water.

Introduction

There is a substantial body of literature and understanding of binding thermochemistry of main-group and transition metal ions to various kinds of ligands. However, as attention moves toward metal ion attachment to larger and more complex molecules, it is increasingly interesting to consider the competitions and possible interactions between binding sites of different character on the same molecule. Subtle differences between different metal ions can assume crucial importance if they create qualitative changes in the preferred site of binding on a given host molecule.

Two ubiquitous types of binding sites are aromatic sites and oxygen sites. We can note a few examples of recent interest in these two types of metal ion binding: there has been much recent comment on the role of cation−π interactions in biological systems,[1−5] while the metal ion/oxygen interaction is central to a great variety of molecular recognition and host−guest chemistry.[6−10]

Phenol is the fundamental prototype for competition between an aromatic π face and an oxygen n-donor basic site. Moreover, the specific competition in this molecule has interest in modeling metal ion binding to peptides, since the phenolic side chain of tyrosine might be a target for metal ion binding to peptide chains. For instance, Hu et al.[11] characterized features in the mass spectrometry of some metal ion/peptide complexes which were clearly due to metal ion interaction with the tyrosine side chain, but they did not specifically decide which of the two sites of the phenolic side chain was responsible for the interaction. The work of Gokel's group on alkali metal binding to tyrosine-containing host molecules[12] gives other examples of recent interest in interactions involving the tyrosine side chain. Confidence in understanding the factors governing questions of site competition as a function of metal ion will be valuable in thinking about such systems.

Binding to biologically interesting sites normally involves both competition between possible sites and also chelation involving binding to multiple sites. In parallel work of our group,[13−16] we have considered the chelating aspects of metal ion/aromatic amino acid interactions, where a metal ion binds an aromatic site, an oxygen site, and usually a nitrogen site simultaneously. In contrast, the present perspective is on systems (relevant to systems such as those of ref 11 noted above) where aromatic and oxygen binding sites do not chelate, but are in simple competition with each other.

Pending future progress in applying spectroscopic techniques for characterizing gas-phase metal ion complexes, computational approaches offer the best currently applicable approach to characterizing binding site competition in ligands like phenol. The present work uses a computational approach to characterize the phenol competition for a number of transition as well as main-group metal ions, and at the same time aims to solidify our confidence in density functional theory (DFT) results using computational protocols which will be readily extendable to much larger ligands in future work. The results are carefully correlated with similarly computed results for the benzene and water model ligands. This comparison can clarify the extent to which binding thermochemistry calculated by DFT for isolated sites is transferable to the phenol system where the two sites are close together on the same molecule.

Phenol has been examined in experimental surveys of Na^+ binding to small molecules,[17,18] and its sodium ion affinity is probably slightly larger (by 1−2 kcal mol^{-1}) than that of benzene, although the uncertain entropy effects make experimental comparisons at this level of accuracy difficult. Moreover, Hoyau et al.[19] studied the sodium binding sites quite thoroughly by computation, as discussed below.

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Our laboratory used the approach of radiative association kinetics to determine binding energies for several metal ions to phenol.[15] These results were supported by DFT/B3LYP calculations. Mg^+ and Al^+ showed acceptable accord between experiment and computation. For Cr^+ the experimental value was much higher, but it was quite uncertain because of the approach to collisional saturation of the radiative association reaction. Comparison of this value with Cr^+/benzene, and with computations, indicates quite clearly that this value is too high. For Fe^+ a lower limit was derived from the experiment which was consistent with the calculations. The present work extends the computational side of this earlier study much farther.

A final question addressed here has interest for future applications of DFT methods to binding questions, namely the choice of a specific functional appropriate for estimating the binding energy differentials between dissimilar binding sites. This investigation focused on two questions: (1) how much dependence is there on the choice of functional, other things being equal, and (2) is there a functional giving a better match to experiment for these two particular binding sites than the popular B3LYP functional?

Computational Considerations and Methods

Choice of Functional and Basis Set. A question of continuing interest in DFT computations is the effect of basis set size. It is frequently said that DFT methods give better results than ab initio methods when the basis set is small. One benchmark for evaluating basis set effects for transition metal calculations is provided by the M^+/H_2O calculations of Irigoras et al.,[20−23] which they performed with both a modest (DZVP) and a large (augmented TZVP) basis (both optimized for DFT). The binding energies were found to decrease systematically using the larger basis compared with the smaller basis. Our comparable B3LYP calculations fell between these two results,suggesting that the basis we used is superior to their DZVP basis, but not as good as the aug-TZVP basis. (Note that in the Fe^+ case, our value came close to their results only after the correction for adiabaticity was made, as discussed below. Our corrected diabatic dissociation value agreed acceptably well with the values they reported.) After correction for zero-point energy (ZPE) and basis set superposition error (BSSE) effects, the H_2O binding energies calculated using these different basis sets do not in general differ by more than 1 or 2 kcal mol^{-1}, which is smaller than other computational uncertainties. As long as the basis is of reasonable quality, this suggests that basis set considerations play a minor role in determining the quantitative reliability of DFT for binding energies of metal ions up to Cu^+ at least. Irigoras et al. also compared the DFT results with coupled-cluster calculations, and found the latter to give lower binding energies usually by several kcal mol^{-1}. The DFT values agreed better with recent experimental results, suggesting that even for such small transition-metal-containing systems there is still doubt about how to calculate accurate absolute binding energies.

There is still enough uncertainty about the true binding energies for nearly all transition metal complexes (except perhaps for some very small ligands) that it is hard to assess the performances of the many alternative DFT functionals. However, some useful comparisons are possible even within the limitations of current uncertainty about the true values. The present work was not at all intended as a survey of DFT functionals, or as a comprehensive test of the B3LYP functional for metal complexes. However, there have been a number of suggestions that the LYP correlation functional, and in particular the still-popular B3LYP hybrid functional which includes LYP, is not optimal for metal-complex calculations, and that other functionals can give distinctly superior results. The frequent poor performance of this functional seems to have led to some perception that DFT methods are unsatisfactory for metal-containing systems. However, judging from at least some recent work, DFT binding energy calculations using the best-performing functional for the class of complexes involved can give results comparable to the best alternative computational approaches, with greater economy. Certainly high-level ab initio computations are preferable when they are feasible, but DFT methods compare well with other computational approaches that can be contemplated for large metal-containing systems.

We can note a few recent studies illustrating this point of view. Stöckigt[24,25] surveyed the effects of changing both basis sets and functionals for the Al^+/benzene system. He found differences of several kcal mol^{-1} between different functionals. The B3LYP functional gave generally low binding energies for Al^+ π complexes, which he attributed to known deficiencies in the LYP functional, whereas the performance of the PW91 correlation functional (in this case, using the BPW91 or B3PW91 hybrid functionals) was satisfactory. For any given functional, the usual difference between the 6-311+g(d) basis and the larger 6-311++g(3df,2p) basis was a small increase in binding energy (about 1 kcal mol^{-1}), which moved slightly closer to the experimental value, but there was essentially no convergence toward a common value for the different functionals. The small 6-31G(d) basis gave values several kcal mol^{-1} higher than the larger basis sets, but the significance of this is uncertain, since BSSE corrections were not made, and it is now well-known that basis sets like 6-31G(d) which do not include diffuse functions are subject to large BSSE effects. These results suggest that the 6-31G(d) basis is inadequate, but that 6-311+G(d) is sufficiently large to come within 1 or 2 kcal mol^{-1} of the large-basis limit. Armentrout and Rodgers[18] found DFT calculations using the B3LYP functional to be inferior to MP2, G2, or CBS approaches for Na^+ complexes, but they found the B3P86 functional to give results of similar quality to these other approaches.

Hoyau and Ohanessian found B3LYP to give Cu^+ binding energies several kcal higher than the most credible values for several n-donor bases[26] and amino acids.[27] They considered HF/MP2 to be superior to B3LYP for Cu^+ complexes, but concluded that (where feasible) the use of CCSD(T) with a large basis set is necessary to obtain reliably accurate binding energies. The limited evidence presented below suggests that these results may expose a particular weakness of the B3LYP functional rather than a general DFT problem, and that the MPW1PW91 functional with a variety of bases, and also the B3LYP functional with π donors, both give more acceptable results for Cu^+ binding. Klippenstein and Yang's DFT/B3LYP study[28] of transition metal binding energetics to several ligands, including benzene and water, found frequent deviations of several kcal mol^{-1} from the most credible experimental or theoretical values. Porembski and Weisshaar considered the performance of B3LYP to be poor for the energetics of some Y[29] and Zr[30] transition states; they considered the results from MPW1PW91 to be satisfactory, and recommended this as the best functional for transition metal complexes. Zhang et al.[31] considered MPW1PW91 to give the best structure results in some Pt complexes, better than B3LYP.

Based on such examples, the use of the PW91 correlation functional, in particular its use as a component of the hybrid MPW1PW91 functional,[32,33] seems often to give among the best

DFT results, and motivated its adoption in the present work as an appropriate target for comparative calculations alongside B3LYP. As described below, MPW1PW91 gave consistently greater preference to ring sites relative to oxygen sites compared with B3LYP, a general trend whose validity was supported for nearly all metal ions by the better agreement of the MPW1PW91 results with experimental results for water and benzene.

Present Methods. The results described here were obtained by density functional calculations using the Gaussian 98 program package.[34] The principal basis set used in this work (which will be called basis "A") was intended to be large and flexible enough to give results within 1 or 2 kcal mol^{-1} of the large-basis limit, while still being small enough to support future extensions to much larger ligands. As judged by comparison with large-basis results and by the small values found for basis set superposition errors (BSSE), the first goal was met. With a basis like this one, current computational capabilities make calculations easily feasible on ligands many times larger than phenol, so this basis seems to satisfy both of our criteria. The A basis: metal, 6-311+G(d); C and O, 6-31+G(d); ring H, 6-31G(d); hydroxyl H, 6-31G(d,p). For comparison, large-basis calculations were made using a basis which will be called the "B" basis: metal, 6-311++G(3df); C and O, 6-311+G(df); H, 6-311G(d,p).

The default metal ion 6-311+G(d) basis sets for Na, Mg, and Al consist of the Maclean–Chandler[35] basis with default polarization and diffuse functions, and those for the transition metals consist of the Wachters–Hay[36,37] basis with scaling factors and diffuse functions as recommended by Raghavachari and Trucks.[38] Calculations with the A basis included full geometry optimization at the level of basis A, while the calculations with the B basis used the corresponding optimized A-basis structures. The A basis was used for the calculations of zero-point vibrational energies (ZPVE), which are not very basis set sensitive.

Geometry optimization to within better than 0.1 kcal mol^{-1} for the ring sites was taken as sufficient to verify the locations of the sites, since there is no better location for the metal ion. However, the O sites, not being global minima, were tested for stability by full vibrational calculations with the A basis to verify (by the absence of negative force constants) that they were true minima on the potential surface. The lowest normal-mode frequency was always low, in the range 20–50 cm^{-1}, but was never imaginary, confirming the stability of the O binding sites.

Although comprehensive calculations of ZPVE and BSSE corrections were not made, some representative systems were checked for BSSE, and many vibrational calculations were completed. For instance, some BSSE counterpoise corrections, using the geometry-consistent approach of Xantheas,[39] were calculated (in kcal mol^{-1}) as 0.3 (Na$^+$ ring site), 0.6 (Na$^+$ O site), 1.0 (Ti$^+$ ring), 0.9 (Ti$^+$ O), 0.6 (Cu$^+$ ring), and 0.8 (Cu$^+$ O). ZPVE values showed little variation, with no significant difference between values for ring sites and O sites, and the average value (based on 16 explicit calculations) was 0.8 ± 0.2 kcal. It seemed that variations in these calculated corrections were small and fairly random, and it seemed justifiable to apply average, generic corrections to all the binding energies rather than relying on the dubious benefit of individual correction calculations. Accordingly, the binding energies calculated here (basis set A) were adjusted downward by 1.5 kcal mol^{-1}. The basis set B calculations were all adjusted downward by 1.0 kcal mol^{-1}. (For water complexes the zero-point corrections are typically somewhat larger than for the bigger molecules, and an additional 0.5 kcal mol^{-1} correction was subtracted in those cases.)

The use of generic, rather than specifically calculated, corrections for BSSE and ZPVE can be criticized, but it is doubtful whether individual counterpoise correction calculations and vibrational frequency calculations are sufficiently accurate to justify such fine distinctions, even if one were to ignore the other more substantial uncertainties in calculations on transition metal systems at this level of theory. Recent discussion suggests that the questions of whether and how to make counterpoise corrections for BSSE in metal ion complexes are far from settled (for instance, ref 40). An additional possibility suggesting caution in interpreting computed values for heavier metals is that of uncorrected relativistic effects. Perturbation estimates of the relativistic corrections to the binding energies of the first-row transition metal cation hydrides led Pettersson et al.[41] to lower these by amounts varying from 0.3 (Ni$^+$) to 2.1 (Cr$^+$) kcal mol^{-1}, although this group has decided not to attempt such corrections for the complexes of interest here.[42,43] Such effects may not be negligible at a precision of 1 or 2 kcal mol^{-1}.

Results and Discussion

Sodium Cation. The binding thermochemistry of Na$^+$ to the ligands of interest here is among the best characterized among metal ion complexes. References 17–19, 40, 44, and 45 give a comprehensive picture of recent experimental and computational understanding of a range of Na$^+$ complexes. The present work does not add very much to the existing understanding of these systems, but it is useful to review the Na$^+$ systems using the present methodology as background for the studies of more complicated metals. Na$^+$/H$_2$O has recent experimental affinities of 21.0 ± 1.5 kcal mol^{-1} (threshold collision induced dissociation (TCID), ref 44) and 21.4 kcal mol^{-1} (ligand-exchange equilibrium, refs 17, 19, converted from measured ΔG and adjusted to 0 K). Computational values with reasonably high levels of theory cover the range from about 21 to 23 kcal mol^{-1} (see refs 17–19 for surveys, and ref 40 for further discussion).

Recent experimental values for the Na$^+$/benzene complex are 22.8 kcal mol^{-1} (TCID, ref 44) and 22.6 kcal mol^{-1} (ligand-exchange equilibrium, ref 17 converted from measured ΔG and adjusted to 0 K). Credible computational values (recently summarized in ref 45) range from about 21.0 to 24.5 kcal mol^{-1}.

Na$^+$ is the only metal ion for which experimental binding energies to phenol by accurate quantitative techniques appear to be available. These are reported as 23.5 kcal mol^{-1} (TCID, ref 18) and 21.5 kcal mol^{-1} (ligand-exchange equilibrium, ref 17, using computational results to convert the experimental ΔG to ΔH, and adjusted to 0 K).

Na$^+$ binds to phenol with clearly distinct ring and oxygen binding neighborhoods, as was carefully described in ref 19. Interestingly, the oxygen neighborhood gives a different binding site geometry for Na$^+$ than for the other more strongly interacting metal ions. Hoyau et al.,[19] using MP2 and a reasonably large basis, located a dipole-bound structure in which the metal ion is apparently held electrostatically at the negative end of the O–H dipole, which in turn is oriented at an oblique angle to the ring plane. The calculated ΔG_{298} of binding was in reasonable agreement with their experimental equilibrium determination[17] (16.7 kcal mol^{-1} measured, 15.4 kcal mol^{-1} calculated). This structure was also the local minimum on the potential surface in the O-binding region of our Na$^+$ DFT calculations, but we found no metal ion other than Na$^+$ for which this structure could be identified even as a local minimum. The geometry of this site using MPW1PW91 DFT is shown in Figure

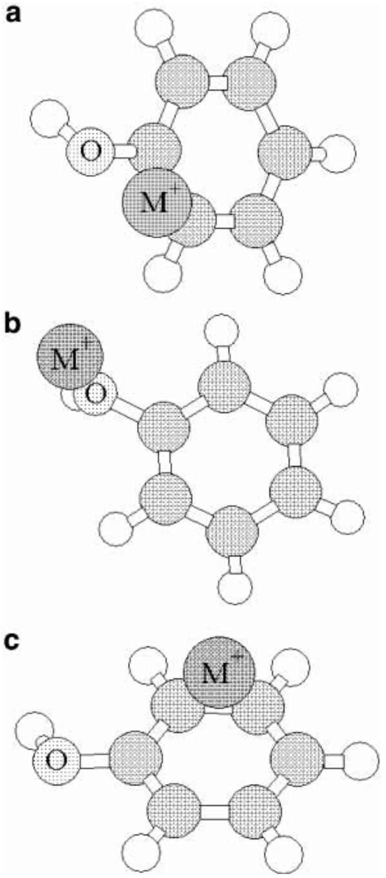

Figure 1. Phenol binding sites for metal ions, showing the Na^+/phenol complexes for illustration (DFT/MPW1PW91). (a) Dipole-bound O site. (b) Trigonal O site. (Note that the MOH plane is perpendicular to the ring plane.) (c) Ring site. (Note that the metal sits over the center of the ring.)

1a. In the calculations of Hoyau et al.[19] the ring site was found to have roughly the same energy as the dipole-bound O site, while the latter site was predicted to have the lowest free energy by virtue of its higher entropy.

It appears that Na^+ does not quite have a stable trigonal oxygen site similar to those discussed below for the other metal ions, with the H−O−Na plane perpendicular to the ring plane. However, the potential surface is very flat in this region, and it is easy to optimize the structure to a high degree of accuracy with the Na^+ ion located at the nearly stable trigonal location similar to the stable geometry exhibited by the other metal ions, as shown in Figure 1b. Finally, the ring-bound site (Figure 1c) is entirely normal, with the metal atom nearly centered over the ring.

TABLE 1: Na^+/Phenol Binding Enthalpies (kcal mol^{-1} at 0 K): Present Results (Using Basis A//Basis A) Except as Noted

	dipole O site	trigonal O Site	ring site
MP2[a] (298 K)	21.9	b	21.8
B3LYP	23.7	23.4[c]	23.4 (22.9[d])
MPW1PW91	23.1	22.6[c]	24.1
B3P86	22.6	22.3[c]	23.4 (22.8[d])

[a] Values from ref 19, adjusted to 0 K by subtracting 0.4 kcal mol^{-1}, following ref 18. [b] The authors did not discuss a trigonal geometry. [c] For Na^+ the trigonal site is nearly, but not quite a local minimum on the potential surface. The energy for this structure is of interest for comparison with the other metals where this is the stable O-binding site. [d] Reference 18. They reported the ring site to be enthalpically the most stable, and did not report energies for other sites.

Table 1 gives a site-by-site comparison of the energies from the different computations. (Independent of methodological questions about DFT, the effect of our relatively small basis makes our values for this complex shown in Table 1 too high by 1−2 kcal mol^{-1}, so the apparent disagreement of DFT and MP2 results in Table 1, on the order of 1 kcal mol^{-1} for the favored B3P86 functional, might be even smaller in a comparison at the complete-basis limit.) Reinforcing the conclusions of Hoyau et al.,[19] our results indicate that Na^+ binding in the neighborhood of the oxygen presents a potential surface that is very flat. The picture from the DFT calculations thus supports their conclusion that the entropy of the oxygen-bound conformation is high. The actual conformational entropy of this "site" is likely to be substantially underestimated by a harmonic approximation: the metal ion can probably traverse a wide, anharmonic and even multiwell region of configuration space around the oxygen at room temperature. We conclude from Table 1 that the ring and oxygen neighborhoods are indistinguishable with respect to Na^+ affinity within the uncertainty of computations at the level of current work.

The absolute DFT binding energies agree acceptably well with the MP2 values of ref 19. For Na^+ the three functionals tested are in reasonable agreement. The MPW1PW91 functional generally tends to favor the ring binding site more than other functionals (by ∼1 kcal mol^{-1} in this case). In accord with Armentrout and Rodgers' more comprehensive observation,[18] the B3P86 results are parallel to B3LYP, but with about 1 kcal mol^{-1} lower binding energies.

It is interesting to compare the phenol binding results with the results of Nicholas and Hay for anisole.[46] They reported ab initio calculations at the MP2 level for all the alkali metal cations with anisole, among which the Na^+ results are pertinent to the present work. Significant BSSE corrections were needed, as is typical of MP2 calculations, 2.1 kcal mol^{-1} for the O site and 3.1 kcal mol^{-1} for the ring site. Binding energies were assigned as 25.4 and 24.0 kcal mol^{-1} for the O site and the ring site, respectively. Just as with phenol, the two sites of anisole are thus close in energy. The ring site was about 3 kcal mol^{-1} more strongly bound than their similar calculation for benzene. Comparing with the phenol calculation of Hoyau et al.[19] at a similar level of theory (Table 1), it appears that anisole is more strongly bound than phenol by 2−4 kcal mol^{-1}, and shows a slightly greater preference for the O site. This small enhancement of the Na^+ affinity of anisole relative to phenol is parallel to the 4 kcal mol^{-1} enhancement of the proton affinity of anisole relative to phenol.[47]

Our results for all the metal ions, including Na^+, are displayed graphically in Figures 2−4, which show the results for the model systems and the results for the phenol sites, and also display directly the differential binding energy between the ring and O sites.

Heavier Metals. *Structures of the Complexes.* The ring-bound phenol complexes were all found by DFT to have stable energy minima with the metal ion approximately over the center of the ring (as modeled in Figure 1c), with the notable exception of Cu^+. For metals other than Cu^+ the metal ion over the ring was normally slightly displaced laterally away from the center of the ring in the direction away from the hydroxyl, by a distance on the order of 0.1 Å. Table 2 shows the distances of the metal ions above the ring (B3LYP). These distances show an overall trend similar to those for benzene, with variations relative to the benzene distances that show no consistent pattern. The MPW1PW91 functional gives a similar pattern, but with metal−ring distances smaller by typically 0.05 Å. The hydroxyl

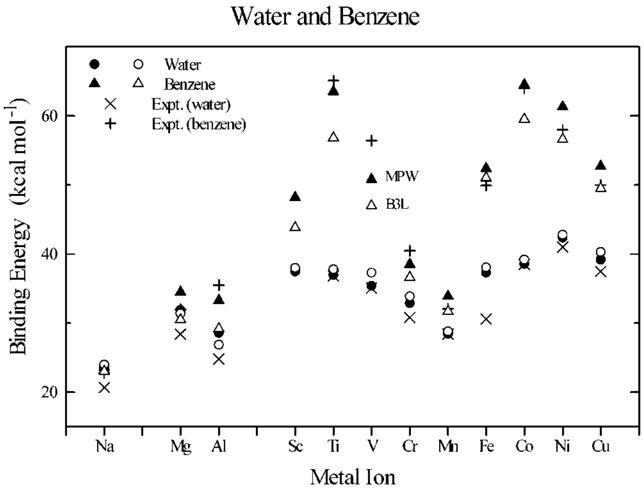

Figure 2. Binding energies to water and benzene. Filled symbols are MPW1PW91 results; hollow symbols are corresponding B3LYP results. Circles are calculated water binding energies, triangles are calculated benzene binding energies, and + (benzene) and × (water) symbols are experimental values. (All data were plotted from Table 3.)

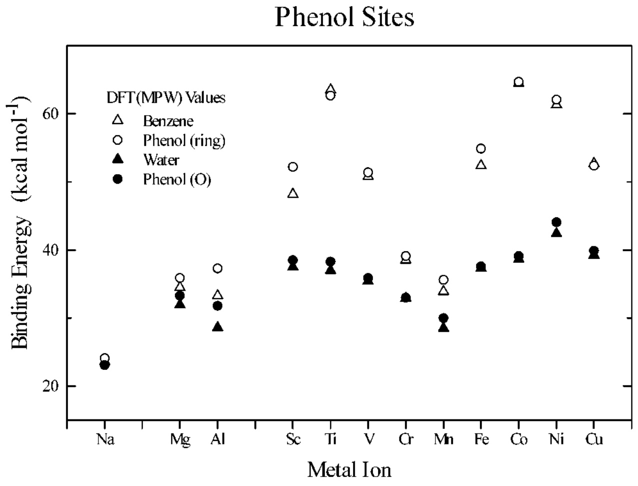

Figure 3. Calculated binding energies to the two sites of phenol, and to the model sites of water and benzene. (DFT/MPW1PW91 results were plotted from Table 3.)

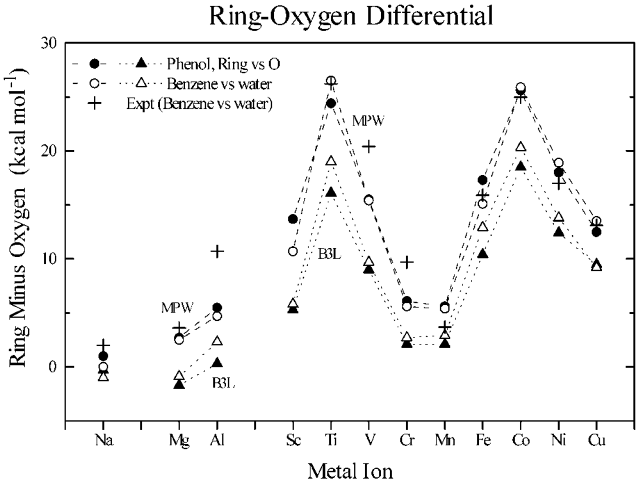

Figure 4. Binding energy differential between ring and oxygen sites. Solid symbols show the differentials for the phenol sites; open symbols show them for benzene versus water model sites. Circles are DFT/MPW1PW91 results; triangles are DFT/B3LYP results. The + symbols show the experimental difference between benzene binding and water binding of the corresponding metal ion. (Data were calculated and plotted from Table 3.)

TABLE 2: Geometrical Parameters of Binding Sites (DFT/B3LYP)

	ring site		trigonal O site		
metal ion	M−ring phenol (Å)	M−ring benzene (Å)	M−O phenol (Å)	angle MOC phenol (deg)	M−O water (Å)
Na	2.39	2.41	2.18	105	2.23
Mg	2.30	2.30	2.03	116	2.08
Al	2.41	2.42	2.02	115	2.09
Sc	1.93	2.18	2.13	117	2.19
Ti	2.04	1.88	2.03	119	2.09
V	1.96	1.94	2.05	117	2.09
Cr	2.14	2.09	2.02	117	2.07
Mn	2.53	2.33	2.12	115	2.16
Fe	1.84	1.80	1.98	120	2.08
Co	1.79	1.66	1.94	117	1.96
Ni	1.75	1.93	1.92	114	1.94
Cu	a	a	1.93	123	1.94

[a] Metal ion migrates to the side of the ring; see text.

hydrogen was always near the ring plane, very slightly displaced away from the metal side of the ring.

In calculations of the Cu^+/phenol complex, both of the DFT functionals showed the Cu^+ moving from the center to the side of the benzene ring, gaining about 1 kcal mol^{-1} relative to the ring-centered structure. The most favorable position for Cu^+ was directly on top of the C_3-C_4 bond (where C_1 designates the hydroxyl-bearing carbon), while the position on top of the C_2-C_3 bond was also favorable, but about 0.5 kcal mol^{-1} less stable than the most favorable geometry. On the other hand, MP2 optimization of this complex with the same basis set gave a ring-centered structure as the most stable. Thus it may well be that the DFT prediction of an off-center position for the ring-bound Cu^+ ion is a DFT artifact.

This question was explored slightly further by reexamining the DFT predictions for Cu^+/benzene. The d^{10} metal ions Cu^+ and Ag^+ clearly have very flat potential surfaces over the benzene ring. Bauschlicher et al.[42] found that Ag^+ has its most stable position at the side of the ring (similar to the structure assigned by DFT in the Cu^+ case), although the energy gained by moving away from C_{6v} symmetry was apparently small. They found the C_{6v} structure for Cu^+ to be stable, and did not discuss the energy cost of moving the Cu^+ ion off center. In the present study the Cu^+/benzene complex was reexamined using both of the DFT functionals and the same basis set as was used in the phenol work. With B3LYP, the structure with the metal ion at the side of the ring (nearly directly over the C−C bond) had exactly the same energy as the ring-centered structure. With MPW1PW91, the ring-centered structure was more stable by 2 kcal mol^{-1} than structures with the metal ion constrained to the side of the ring, and in fact no local minimum was found off center. The DFT results thus give no reason to reconsider Bauschlicher's assignment of a ring-centered structure for the Cu^+/benzene complex, but they show that a very flat potential surface allows easy movement of the metal ion away from the center of the ring. Apparently in the case of phenol, interaction with the OH group makes the off-center geometries slightly more favorable than for benzene. Whether the global energy minimum for the Cu^+/phenol ring-bound complex is actually ring-centered or off center is not discernible within the uncertainty of the present calculations.

As a further test of late transition metal ions, the tendency of the Ni^+ ion to move away from the center of the benzene ring was also investigated with the Ni^+/benzene complex. Off-center structures were less favorable than with Cu^+, and it costs

TABLE 3: Comparison of Phenol with Model Sites[a]

		phenol (ring)		benzene		phenol (O)	water	
metal ion		DFT	expt (phenol)[b]	DFT	expt (benzene)	DFT	DFT	expt (water)
Na	MPW	24.1	23.5, 21.5	23.6	22.8 ± 1.5,[c] 22.6[d]	23.1	23.6	21.0 ± 1.5,[c] 21.4[d]
	B3LYP	23.4		23.0		23.7	24.0	
	B3P86	23.4		22.4		22.6	23.3	
Mg	MPW	35.9	38.2	34.5	32 ± 2[e]	33.3	31.9	28.4 ± 3.6[f]
	B3LYP	31.6		30.5		33.3	31.4	
Al	MPW	37.3	37.5	33.3	35,[g] 36[h]	31.8	28.6	24.8 ± 3.0[f]
	B3LYP	30.7		29.2		30.4	26.9	
Sc	MPW	52.2		48.2		38.5	37.5	30.6[i]
	B3LYP	45.1		43.8		39.8	38.0	
Ti	MPW	62.7		63.5	60.8−65.1[j]	38.3	37.0	36.8 ± 1.4,[k] 37.1[i]
	B3LYP	56.4		56.8		40.3	37.8	
V	MPW	51.4		50.8	54.4−56.4[j]	35.9	35.4	35.1,[k] 35.5,[i] 34.4[l]
	B3LYP	47.6		47.0		38.6	37.3	
Cr	MPW	39.1	49	38.5	40.5 ± 2.5[j]	33.0	32.9	30.8,[k] 28.1,[i] 21.0[l]
	B3LYP	37.7		36.6		35.6	33.9	
	B3P86	42.1		41.5		35.5	34.8	
Mn	MPW	35.6		33.9	32.1[j]	30.0	28.5	28.4,[k] 25.8,[i] 27.8[l]
	B3LYP	33.2		31.7		31.1	28.8	
Fe[m]	MPW	61.1; *54.9*	>57	58.1; *52.4*	43.5−49.9[j]	37.6	37.3	30.6,[k] 27.9,[i] 31.9[l]
	B3LYP	56.3; *50.1*		56.7; *51.0*		39.7	38.1	
Co	MPW	64.7		64.5	62.6−64.0[j]	39.1	39.2	38.5,[k] 36.3,[i] 39.3[l]
	B3LYP	59.7		59.5		41.2	38.6	
Ni	MPW	62.1		61.3	57.5−58.0[j]	44.1	42.4	43.0,[k] 35.6,[i] 38.8[l]
	B3LYP	58.1		56.6		45.7	42.8	
Cu	MPW	52.4		52.7	50.6[j]	39.9	39.2	37.5,[k] 34.1[i]
	B3LYP	51.5		49.5		42.0	40.3	
	B3P86	54.7		55.1		42.0	40.9	

[a] Binding enthalpies at 0 K in kcal mol^{-1}. [b] Experimental values for Na^+/phenol by TCID from ref 18 and by ligand-exchange equilibrium (derived from the experimental ΔG_{298}) from refs 17 and 19; for the other metals, by radiative association kinetics from ref 15. [c] Reference 44. [d] Derived from the experimental ΔG_{298}.[17,19] [e] Reference 49. [f] Reference 48. [g] Reference 51. [h] Reference 24, derived based on ref 50. [i] Reference 61 adjusted to 0 K. [j] Reference 62, which reanalyzed data from ref 59. The ranges of values given correspond to different plausible assumptions in the reanalysis of the original data. [k] References 6 and 63. [l] Reference 64 adjusted to 0 K. [m] For the ring sites, the plain text numbers are spin-nonconserving adiabatic values; italic numbers are spin-conserving dissociation on the quartet surface. For the O sites, all the values refer to low-spin (quartet) species.

the Ni^+ ion about 5 kcal mol^{-1} (MPW1PW91) to move to a similar off-center position. Moreover, the Ni^+/phenol complex showed no tendency for the metal ion to move away from the ring center.

All of the metal ions showed stable local minima at the trigonal O site, as modeled in Figure 1b. The barrier to movement between the sites was not calculated, but in no case was there any sign of migration from the vicinity of the trigonal O site toward the more stable ring site. The coordination around the oxygen was always strictly planar, and the M−O−H plane was always perpendicular to the ring plane. Various attempts to locate stable dipole-bound structures similar to the Na^+ structure of Figure 1a were unsuccessful.

Table 2 gives structural information for the trigonal O sites. The O−metal distances are slightly shorter than those for the water complexes. The M−O−C_1 angle, which would be expected to approximate 120° for a purely sp^2 oxygen, was nearly always less than that, although we see no obvious pattern in the variation of this angle. The exceptionally small value of this angle for Na^+ (which is commonly considered to be bound by nearly pure electrostatic forces) suggests that the electrostatic potential minimum lies at an angle around 105°, and we speculate that the binding of the metal ions other than Na^+ reflects coordination via an sp^2 hybridized oxygen (120°), to which is added an electrostatic perturbation tending to close the M−O−C angle by a few degrees below 120°. In any case, this angle is not tightly constrained and typically varies by several degrees depending on basis set, functional, and other details of the calculation.

Mg^+ and Al^+ Binding Energies. Experimental binding energies (Table 3) have been derived from TCID measurements forAl^+/H_2O,[48] Mg^+/H_2O,[48,49] and Mg^+/C_6H_6.[49] For Al^+/C_6H_6, values derived from experimental data have been given based on extrapolation[24,50] and based on radiative association kinetics.[51]

Previous computational results for these complexes generally range within a few kcal mol^{-1} of the experimental values. Mg^+/H_2O was calculated by Sodupe and Bauschlicher[52] as 31.2 kcal mol^{-1} and by Anderson et al. by MP2 as 28.3 kcal mol^{-1}, while a G2 value of 30.2 kcal mol^{-1} was given recently.[53] The present value (31.9) from our preferred DFT/MPW1PW91 protocol appears to be slightly high compared with these values and with experiment.

For Mg^+/C_6H_6, Partridge and Bauschlicher reported 30.4 kcal mol^{-1} by SCF[54] (which they expected would increase in a higher level calculation); Andersen et al.[49] reported 31.5 kcal mol^{-1} by MP2. The present result (34.5 kcal mol^{-1}) from our preferred DFT/MPW1PW91 protocol is somewhat high compared with these values and with experiment. Thus for both water and benzene, the present MPW1PW91 results with the modest basis used here for Mg^+ complexes are slightly higher than the most credible experimental and theoretical values.

For Al^+/H_2O, Sodupe and Bauschlicher[55] calculated a value of 27.0, while the recent G2 value[53] is 26.1 kcal mol^{-1}. The present DFT/MPW1PW91 value of 28.6 thus appears slightly high relative to experimental and good theoretical values.

Stöckigt surveyed several computational methods for Al^+/C_6H_6,[24,25] obtaining results ranging as much as 5 kcal mol^{-1} on either side of the experimental values. The G2 value of 35.6 kcal mol^{-1} provides a computational reference point. MP2 even with a large basis is high (39.1 kcal mol^{-1}) but would improve if BSSE were corrected. DFT/B3LYP is poor, giving 30.5 kcal mol^{-1} using a large basis even without subtracting BSSE. His DFT/B3PW91 calculation (34.5 kcal mol^{-1} with a basis comparable to ours) is quite similar to the present DFT/MPW1PW91 value (33.3 kcal mol^{-1}), and would actually be almost the same if it were corrected for BSSE. His DFT/B3PW91 results with a large basis (36.0 kcal mol^{-1} without BSSE correction) is in very good agreement with G2, which supports the idea that DFT calculation using the PW91 correlation functional is capable of acceptable computational performance for Al$^+$ complexes.

As shown by Table 3 and the figures, there is substantial variation in the present DFT results for Mg$^+$ and particularly Al$^+$, depending on the functional chosen. The tendency of the B3LYP functional to give a smaller ring/oxygen differential than the MPW1PW91 functional is clear in Figure 4. Agreement with experiment for water and benzene is generally adequate, given a realistic uncertainty of several kcal mol^{-1} on the experimental numbers. However, since these Al$^+$ and Mg$^+$ complexes are now accessible to high-level ab initio calculations with large basis sets, DFT calculations are probably not the preferred approach to predicting absolute binding energies in these cases. We have more confidence in the DFT predictions of the ring/O differential, particularly the MPW1PW91 results.

There is quite a large and unexpected difference in the experimental ring/O differentials displayed in Figure 4 for the Mg$^+$ case (3.6 kcal mol^{-1}) versus the Al$^+$ case (10.7 kcal mol^{-1}). This discrepancy is not supported by the present calculations; moreover, theory consistently gives reasonably similar binding thermochemistry for these two metal ions, so we suspect that this experimental differential is not real, but rather a reflection of the large uncertainties still present in the available experimental thermochemistry. Mg$^+$ probably has a ring/O differential larger than that for Al$^+$ by 2−3 kcal mol^{-1}.

As is clear in Figure 4, ring and oxygen binding sites for these two metal ions are not far apart in energy. The B3LYP results suggest that Mg$^+$ prefers O sites over ring sites, but the MPW1PW91 results, indicating a small preference for ring sites, are probably more credible. Even so, the O site of phenol for Mg$^+$ may well be thermally populated at ordinary temperatures, particularly if it is entropically favored as it is for Na$^+$. (In the absence of differential entropy effects, a site lying 1 kcal mol^{-1} higher in energy than the most stable site will be about 20% populated.) For Al$^+$, the enthalpic advantage of the ring site over the O site is larger, on the order of 5 kcal mol^{-1}, and significant thermal population of the O site seems less likely with this metal ion.

Correlating computed results with experiment, Figure 4 gives a clear graphical demonstration of a general conclusion of this work, that the MPW1PW91 functional (circles) does a better job of predicting the binding energy difference between water and benzene than does the B3LYP functional (triangles). Carrying this observation over to the case of phenol (where the differential between the sites is not experimentally verifiable), we give a strong preference to the MPW1PW91 functional for the purpose of comparing the ring and O sites, and will largely base our discussion and conclusions for all the metals on the results from this functional (except Na$^+$, where the functionals seem to be similar).

Transition Metal Ion Binding Energies. The framework of understanding binding in transition metal ion complexes of both oxygen bases and aromatic rings was laid out by Bauschlicher et al.[42,43,56,57] in a classic series of papers extensively drawn on by later workers (for instance, refs 6 and 58). An important aspect of this is the interplay of interactions and promotions involving the 3d and 4s valence electrons of the metal. The DFT methods underestimate the stability of the 4s orbital relative to the 3d orbitals, which leads to some problems in treating metal ion complexes in those cases where there is the possibility of a change in configuration between the bare ion and the complex. These questions were reviewed by Klippenstein and Yang.[28] The most serious uncertainties arise for Ti$^+$ and Fe$^+$, for which DFT methods give the wrong ground state configuration of the bare metal ion. For Fe$^+$ the problems are particularly severe because DFT predicts a low-spin (quartet) ground state instead of the actual high-spin (sextet) state.

The poor ability of DFT to calculate binding processes involving configuration changes was addressed by Klippenstein and Yang[28] by the procedure of calculating a diabatic dissociation of the complex to the bare metal ion having the same configuration, and then correcting the resulting dissociation energy using the experimental energy difference between this metal ion state and the actual metal ion ground state. For dissociations where spin change is not an issue (all except Fe$^+$), this approach was not attractive in the present work for the phenol complexes, because mixing of the 3s and 4d orbitals frequently made the identification of the configuration of the complex ambiguous. Accordingly, all our results (except for Fe$^+$) are reported for the apparent adiabatic processes, in which the DFT ground state of the complex is dissociated to the DFT ground state of the bare metal ion. This difference in method contributes to the differences between the DFT energies given in Table 3 and those assigned in ref 28 (although these effects are minor except for Ti$^+$). It is arguable whether our adiabatic calculations give less reliable binding energies than the corrected-diabatic approach of ref 28 for water and benzene, but it seemed better in any event to use a uniform approach for all our calculations in order to make valid correlations with phenol.

Fe$^+$ poses a particularly difficult computational (as well as experimental) problem with benzene ring ligands, because the dissociation of the metal ion from the ligand is accompanied by both a change from 3d^7 to 3d^6 4s^1 orbital occupation and a change from low spin (quartet) to high spin (sextet). The spin change means that the ligand affinity calculation involves comparing computations on different spin manifolds, which are particularly difficult and method-dependent comparisons. It is even uncertain whether a given experimental result will reflect the true adiabatic ligand affinity of Fe$^+$, since an experimental dissociation process cannot be assumed to proceed with fully adiabiatic change of spin. Adding more uncertainty to making the comparison of the two binding sites is that DFT (correctly) predicts the ring sites to be low-spin d^7, while it (incorrectly) also predicts the O sites to be low-spin d^7, so direct comparisons of DFT numbers for the two sites may be misleading. Klippenstein and Yang's approach to estimating the Fe$^+$ affinities used DFT to calculate the diabatic dissociation on the quartet surface (quartet to quartet) in all cases, and then the dissociation energy was adjusted for the spin-changing cases using the experimental excitation energy of the quartet-state iron ion. This same procedure was followed here to give corrected diabatic binding energies. Given these various uncertainties, Fe$^+$ binding thermochemical values, both experimental and calculated, should be interpreted with caution.

All of the binding energies calculated are displayed in Table 3, along with comparative values for the two model sites. It is clear that the two sites of phenol correspond closely to the comparably calculated metal ion affinities of the benzene and water model sites. Thus the periodic trends and discussions of

TABLE 4: M$^+$/Phenol Large-Basis Binding Energies (Basis B//Basis A)[a]

metal		ring-bound	O-bound
Mg$^+$	MPW1PW91	36.1 (35.9)	33.7 (33.3)
	B3LYP	31.5 (31.6)	33.9 (33.3)
Mn$^+$	MPW1PW91	35.6 (35.6)	30.1 (30.0)
	B3LYP	32.6 (33.2)	31.0 (31.1)
Cu$^+$	MPW1PW91	51.9 (52.4)	39.9 (39.9)
	B3LYP	51.2 (51.5)	42.9 (42.0)

[a] Values in parentheses are smaller-basis values taken from Table 1.

binding to water and benzene in the literature (for instance, refs 6, 24, 42, 43, 48, 49, 59, and 60) are completely applicable to the phenol binding sites.

The systematic electronic effects governing binding with these model ligands are well-known and understood, but it is interesting to display them graphically, illustrating how the same effects carry over to the two sites of phenol. Figure 2 compares the computed values with our best estimates of the experimental values for water and benzene. It is evident that much of the large variation in ring/O differential energies as we go across the transition metal series (Figure 4) arises from the variation in ring binding, and thus traces back to the large electronic effects governing the interactions of the ring π system with the metal valence orbitals. The variations in oxygen binding are almost insignificant: O binding shows a modest dip in the region of Cr$^+$, Mn$^+$, and Fe$^+$. In comparison with the metals to the left of Cr$^+$, this reflects mutual repulsion of the d_{z^2} electron and the oxygen lone pair, while for Mn$^+$, and perhaps for Fe$^+$, repulsion between the ligand and the occupied metal 4s orbital is also unfavorable to O binding. However, the modest variations in O binding are much less dramatic than the variations seen in benzene ring binding, which clearly reflect the large additional interactions arising from the $\pi-$d donation and d$-\pi^*$ back-donation interactions between the metal and the ring.

Table 3 and Figures 2−4 show that for most transition metal ions studied the ring site is beyond doubt more favorable than the O site. If we accept the B3LYP predictions (which we do not consider reliable), and further postulate a substantial entropic favoring of the O site similar to that calculated in the Na$^+$ system (on the order of 1 kcal mol^{-1} at 300 K),[19] there is a possibility for Cr$^+$ and Mn$^+$ that the O site might be thermally accessible in competition with the ring site. The MPW1PW91 results are less favorable to O-site binding, and indicate that this site is not likely to be thermally populated. However, it is interesting to note that the experimental comparison of benzene and water affinities for Mn$^+$ indicates a rather small differential, and by itself could indicate substantial thermal competition between the two phenol sites for this metal ion. It is the generally good success of the MPW1PW91 approach reflected in Figure 4 that leads us to believe that this experimental comparison is misleading, and that Mn$^+$ follows its neighbors in having a marked preference for ring-site binding. For transition metal ions other than Cr$^+$ and Mn$^+$, the O site is clearly beyond reach in any thermally equilibrated situation.

Performance of the DFT Calculations. The present work did not attempt a comprehensive survey of basis set effects for phenol, but it seemed interesting to to test a few systems to see whether our usual “A” basis was adequate to approach the large-basis limit. Table 4 shows a few results using our larger “B” basis. Comparing with the “A” basis, it is seen that the differences are small, mostly less than 1 kcal mol^{-1}. The differences between the two functionals were not significantly reduced by increasing the basis, and the differences between the ring and oxygen binding sites also remained essentially the same. Accordingly, it did not seem likely that basis set inadequacy would endanger any of the principal conclusions of this study.

The finding of Armentrout and Rodgers[18] that the B3P86 functional gave Na$^+$ binding energies about 1 kcal mol^{-1} lower than B3LYP, agreeing with experiment virtually as well as any of the computational methods that they surveyed, raised the possibility that this functional might also prove useful for transition metal complexes. Guided by this suggestion, trials of B3P86 were made for Cr$^+$ and Cu$^+$. However, the predicted binding energies for these two examples seemed to be clearly too high (Table 3), and this line of exploration was not followed further for other metal ions.

Although the DFT predictions of absolute binding energies to phenol may have some interest, it is the competition between the two binding sites, and the relative performance of the different DFT functionals in modeling this competition, that is the focus of attention of the present study. A comparison of the two functionals can be made using the values for water, benzene, and phenol displayed in Table 3. We would like to use the experimental values as benchmarks for the true absolute and relative values, although they are still rather uncertain. The highly regarded calculations of Bauschlicher’s group,[42,43] at a high theoretical level, give additional support to the experimental values in many cases. The most obvious generalization, comparing B3LYP and MPW1PW91, is that binding to the aromatic ring is predicted to be consistently stronger by MPW1PW91 than by B3LYP, while binding to oxygen does not show large or consistent differences. This leads to a very pronounced difference in the predicted relative energies of the two sites, as displayed in Figure 4. The figure shows the relative binding energies of the ring and the oxygen, both for the phenol two-site system, and also for the benzene/water models. It is clear that for all metals the MPW1PW91 results give a more favorable ring/O differential than the B3LYP results.

Looking at the available experimental results as displayed in Figure 4, we can conclude tentatively that the MPW1PW91 functional gives a better estimate of the ring/O differential than B3LYP. Given the substantial experimental uncertainties assigned by their authors to the experimental values (even in the cases where there are no methodological uncertainties in the data analysis), the match between the MPW1PW91 results and the experimental ring/O differentials is good. This bolsters our confidence in the theoretical predictions for the competition of the sites in phenol, where no experimental verification is possible.

DFT calculations are not the approach of choice for accurate absolute calculations of metal ion affinities of small systems. The benzene and water ligands have already been treated at higher levels of theory for most or all of the metal ions considered here, and phenol is certainly now accessible to calculations at a very high theoretical level. Thus the absolute values by DFT presented here may be useful for cases where better calculations are not yet available, but are not presented as definitive. On the other hand, the present results show credibility for quantitative DFT comparisons of these competing binding sites, and the conclusions reached here about the relative site affinities should be robust. Furthermore, the finding that the benzene/water comparisons closely mirror the competing site comparisons for phenol supports the hope that this approach will be quantitatively accurate for similar site comparisons in much larger molecules.

Conclusions

For most of the transition metal complexes from Sc$^+$ to Cu$^+$, the ring site is unequivocally favored energetically over the O site, by such large increments that the O site cannot be thermally populated at any reasonable temperature, regardless of the choices made in computing the predicted binding energies. Mn$^+$ is an intriguing possible exception, since the B3LYP computations, more or less supported by experimental information, can justify placing the O site in phenol not far above the ring site in energy. It is thus possible that the O site is thermally accessible to Mn$^+$. The B3LYP results raise a similar possiblity for Cr$^+$, but in this case the experimental observations weigh strongly against O-site binding, and it seems unlikely that the phenol O site is thermally accessible to Cr$^+$. However, it should be stressed that we consider the B3LYP calculations to be unreliable for this purpose, and do not consider these possibilities to be realistic. The MPW1PW91 calculations, in which we put more confidence, generally indicate a less favorable competition for the O sites, and make it unlikely that this site is thermally accessible for any transition metal ion, even Cr$^+$ or Mn$^+$.

For Mg$^+$ in particular, and for Al$^+$ with lower likelihood, the B3LYP values suggest the possibility that the O site of phenol could be the energetically favored site. However, this possibility is not considered likely, because the preferred MPW1PW91 calculations, supported by correlation with experimental results for the model compounds, are less favorable to O-site binding. Based on the MPW1PW91 results, the O site of phenol is probably about 2 kcal mol^{-1} disfavored relative to the ring site for Mg$^+$, and thus might have some thermal population, particularly if the O site is entropically favored as it is for Na$^+$. For Al$^+$ the O site of phenol is probably 5 kcal mol^{-1} disfavored, and is less likely to be thermally accessible.

The DFT methodology applied here gives encouraging results for the transition metal ion complexes. There is good consistency between the phenol sites and the corresponding results for the model sites (benzene and water). For binding to the water model site, differences between the different DFT functionals are generally minor, and there is no good indication of a preference between them. However, the MPW1PW91 functional gives consistently stronger benzene binding than the B3LYP functional, and these higher values are strongly supported by the experimental results. As a consequence of this, the differential binding between ring and O sites is consistently higher by an amount on the order of 5 kcal mol^{-1} with MPW1PW91 than with B3LYP, again with the MPW1PW91 differential values receiving strong support from experiment. For the future, DFT/MPW1PW91 calculations with a modest basis set seem well suited for evaluating binding competition between aromatic ring and hydroxylic oxygen sites for the series of metal cations explored in this work.

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