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Ab Initio Calculations of Monosubstituted (CH_3OH, CH_3SH, NH_3) Hydrated Ions of Zn^{2+} and Ni^{2+}

Lubomír Rulíšek* and Zdeněk Havlas

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic

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Model complexes of hydrated zinc(II) and nickel(II) cations with one water substituted for methanol, methanethiol, and ammonia are studied. The accuracy of various computational methods, influence of the basis set, and the role of the coordination geometry are investigated. It is shown that density functional theory calculations (B3LYP functional) yield very accurate results, but the basis set of at least triple-ζ quality with polarization and diffuse functions should be used. The calculated mean absolute difference between DFT and QCISD(T) reaction energies for the substitution reactions on the central metal ion is less than 0.5 kcal mol^{-1}. It is also observed that the metal−ligand distances and the reaction energies of monosubstituted hydrated complexes of metal ions are strongly dependent on the number of ligands in the first coordination sphere and the coordination geometry. The implications of having a reliable, accurate, and relatively fast method for the calculation of transition metal complexes are discussed. Several applications oriented toward the interactions of transition metals with the amino acid residues are mentioned.

Introduction

Transition metal complexes are systems that challenge any quantum chemical theory. The precise ab initio calculations are very demanding, owing to several aspects that make transition metals unique among the other elements in the periodic table.

(i) One aspect is the high number of electrons, even for the first row, and significant relativistic effects for the second and third rows of transition metal elements (which implies that all electron nonrelativistic calculations are meaningful only for the former, while the relativistic pseudopotentials or relativistic calculations should be used for the latter).

(ii) Another aspect is the partial occupation of valence d-orbitals (substantially determining the chemical behavior of particular transition metal). Except for d^{10} ions (e.g., Zn^{2+}, Cd^{2+}, Hg^{2+}), d-shells of other transition metals contain unpaired electrons and the ground electronic states have usually higher multiplicities. It complicates the calculation in several ways. The ground electronic states may not be necessarily described by the single determinant (electron configuration), and only methods, such as MR-SCF, CI-SD or MR-CI, can give, in principle, correct results. Even if the molecular state is satisfactorily described by the single determinant, the computational cost of an unrestricted open-shell calculation is approximately twice as high than that of the corresponding restricted closed-shell calculation. Then, it is a generally worse convergence of the SCF procedure itself (due to the mixing of d-orbitals), which further increases the computational cost. And finally, the theoretical method should be able to treat equally s^2d^n, sd^{n+1}, and d^{n+2} configurations, as each of them may play an important role in the molecular electronic state. It is most important for the first row transition metal ions, where the compact 3d shell and more diffuse 4s shell exhibit a large difference in their spatial extent.

(iii) When the interaction energy of transition metals with other species is computed (e.g., biologically important functional groups or reagents in catalysis), the spatial requirements of a metal should be satisfied. It means that a metal should be placed in the target coordination geometry and all of its coordination bonds saturated. Most usually, neutral species, such as water molecules (in ionic complexes) or carbonyls (in organometallics), are coordinated to the central metal ion together with the molecule of interest. It again substantially increases the size of the system and the computational cost.

Despite the above theoretical obstacles, the significance of transition metals in chemistry is immense[1] (organometallic and bioinorganic chemistry, organic catalysis, etc.), and so is the need of having reliable and precise theoretical methods for their calculation.

Only in the past decade has it become feasible to perform accurate quantum chemical calculations on the transition metal complexes containing more than two other heavy atoms. Nowadays, there are many papers[2−35] and several excellent reviews[36−40] dealing with the ab initio calculations of the TM complexes.

Several general conclusions can be drawn from the above studies.

(i) In many cases, the ab initio methods can achieve the accuracy that even challenges the experiments.

(ii) DFT methods (especially gradient-corrected functionals) yield very good results for relatively low computational cost. Among other methods, the modified coupled pair approach (MCPF), parametrized configuration interaction (e.g., PCI-80), or second order multiconfigurational SCF (usually denoted as CASPT2) is often successfully used in the more complicated cases (e.g., near-degenerate molecular electronic states).

(iii) Organometallic complexes in which the bonding is governed by the donation and back-donation mechanisms (and high redistribution of electrons) are more difficult to model accurately.

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* Corresponding author. E-mail: lubos@uochb.cas.cz. Telephone/fax: +420-2-20183292.

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(iv) Most of the studies were done for the [metal ion−molecule] systems, where the experimental data are available and the agreement between theory and experiment was often excellent.

Furthermore, there is a growing number of calculations performed on the model transition metal complexes mimicking the biologically relevant systems, though only compounds containing the closed-shell ions (e.g., Zn^{2+}, Cd^{2+}, Hg^{2+}) were studied.[41]

In our work, we address the problems encountered when modeling the transition metal centers and their interaction with the different functional groups attached to it in the defined coordination mode. These are the selection of a computational method, the extent of the basis set needed to obtain the convergence of binding or interaction energies, and the role of the target coordination geometry. We particularly examine the applicability of B3LYP nonlocal hybrid functional, as it seems to work well for many smaller systems and organometallic complexes.

Since the experimental values of the interaction energies of the systems used in this study are not available, we have carried out QCISD(T) and CCSD(T) calculations in the given basis set to obtain the reference values. The structures closely related to the computed ones can be found in Cambridge Structural Database and are compared with B3LYP optimized geometries. Together, it can help to further establish DFT as a practical and relatively fast method for the miscellaneous calculations related to the transition metal complexes of ionic character. In this respect, it is the continuation of the work done by Åkesson et al.[18] They have studied the hexaaqua ions of first and second row transition metals. The calculations were done basically at the SCF level, and they obtained satisfactory results.

The whole study is also motivated by the effort to evaluate precisely the small differences in interaction energies of transition metals with biologically important ligands and to discover the factors determining their affinity and selectivity toward the particular metal. The selected functional groups serve as the models for the interactions of transition metals with the amino acid residues. We hope that the accurate methods of theoretical chemistry may ultimately lead to the understanding of the processes governing the mechanisms of the metal coordination in biological macromolecules.

Methods

We have studied the following substitution reactions

$$[Me(H_2O)_n]^{2+} + Y \rightarrow [Me(H_2O)_{n-1}(Y)]^{2+} + H_2O \quad (1)$$

where Y = CH_3OH, NH_3, CH_3SH, Me = Ni (n = 6), Zn (n = 1, 4, 6).

The zinc(II) cation and its complexes represent closed-shell systems, while nickel serves as the representative of a transition metal with unpaired electrons in its valence shell. Water molecules (in octahedral arrangement) simulate the effect of the solvation of metal and fulfill the role of the saturating agent for the metal coordination bonds (in all arrangements). The three substituents were chosen to mimic the interaction of amino acid residues (Lys, Ser, Cys) with the metal ion.

The ground electronic states of both $[Ni(H_2O)_6]^{2+}$ and $[Ni(H_2O)_5(Y)]^{2+}$ complexes have been examined using the CAS SCF method.[42] The (8,5) active space consisted of five molecular orbitals with a dominant contribution of metal d-orbitals (t_{2g} and e_g MOs in ideal octahedral ligand field). Zn^{2+} has all its five d-orbitals occupied, and therefore, it was not necessary to carry out CAS SCF calculation.

The hybrid three-parameter functional developed by Becke,[43] which combines the Becke's gradient-corrected exchange functional and the Lee−Yang−Parr and Vosko−Wilk−Nusair correlation functionals[44] with part of the exact Hartree−Fock exchange energy, has been used for the calculation (denoted as B3LYP).

The quadratic configuration interaction method[45] with singles, doubles, and noniterative triples (QCISD(T)) has been used to obtain the reference values. One coupled cluster calculation[46] (CCSD(T)) has been carried out as well to confirm the consistency of QCISD(T) and CCSD(T) because of the reported failure of QCISD(T) for Cu−C dissociation energy of $CuCH_3$.[11]

All the calculations were performed with the Gaussian 94 program suite.[47]

Three basis sets were used throughout the calculations: (a) 3-21G,[48] (b) combined double-ζ basis set of Rappé and Goddard[49] on transition metals with 6-31G[50] on other atoms (denoted as DZ), and (c) valence triple-ζ 6-311G.[51] With DZ and 6-311G basis sets, the p,d (H), d,f (C, O, N, S), and f,g (Zn, Ni) sets of polarization functions and s (H), sp (C, O, N, S), (s2pd) (Zn, Ni) diffuse functions were used.[52,53]

Results and Discussion

Equilibrium Geometries. In the first step, the molecular geometry of all participating species has been fully optimized at the B3LYP/6-311+G(d,p) level to obtain the equilibrium geometries that can be used for the subsequent calculations. If any of the computed Ni^{2+} complexes turns out to be a multireference problem, this step needs to be revised and MR-SCF optimization applied. But from the occupation of t_{2g} and e_g sets of orbitals in ligand field theory and from the work of Åkesson et al.,[18] it could be anticipated that Ni^{2+} octahedral complexes can be described by a single electron configuration.

In the second step, CAS SCF calculations (6-311+G(d) basis set) of all $[Ni(H_2O)_6]^{2+}$ and $[Ni(H_2O)_5(Y)]^{2+}$ complexes were carried out at the above optimized geometry. The active space consisted of the five occupied molecular orbitals with the dominant contribution of the metal d-functions. They were identified as the perturbed t_{2g} and e_g MOs coming from the octahedral ligand field splitting, retaining the character of metal d-orbitals (due to the mainly ionic nature of the complexes). The calculations verified the above hypothesis and showed that the ground electronic states (triplets for Ni^{2+} octahedral complexes) of all species can be described satisfactorily by a single determinant. The coefficient of the leading configuration was virtually 1. The usage of the single-determinant methods is justified.

Then we have carried out a series of B3LYP optimizations of $[Me(H_2O)_6]^{2+}$ complexes to determine the extent of basis set needed to obtain the precise molecular geometries. The optimized geometries are depicted in Figure 1, and the results of optimizations in various basis sets can be found in Table 1. It should be pointed out that owing to the worse convergence of the wave function (density matrix) during SCF iterations, it is recommended to use the wave function calculated at the lower level (e.g., 3-21G, STO-3G) as the initial guess for the calculations in DZP and higher basis sets.

As can be inferred from Table 1, the most sensitive geometry parameter is the metal−ligand bond distance. It is poorly described at the B3LYP/3-21G(d) level. However, DZP and higher basis sets produce good results. It is not surprising that addition of polarization functions improves the values of bond angles, while the addition of diffuse functions helps to describe the coordination environment around the metal ion. The other

TABLE 1: Optimized Parameters of $[Me(H_2O)_6]^{2+}$ Complexes, Calculated at the B3LYP Level Using Various Basis Sets

	$[Ni(H_2O)_6]^{2+}$			$[Zn(H_2O)_6]^{2+}$		
basis set	r_{NiO} (Å)	r_{OH} (Å)	α_{HOH} (deg)	r_{ZnO} (Å)	r_{OH} (Å)	α_{HOH} (deg)
3-21G(d)	2.013	0.990	109.0	2.017	0.992	108.6
DZP	2.062	0.968	108.3	2.082	0.969	107.1
6-311G	2.063	0.969	111.6	2.091	0.970	111.1
6-311G(d)	2.066	0.964	108.9	2.097	0.965	108.4
6-311G(d,p)	2.067	0.965	107.9	2.098	0.966	107.4
6-311+G(d)	2.077	0.966	108.6	2.119	0.966	108.3
6-311+G(d,p)	2.087	0.967	108.0	2.129	0.967	107.5
6-311++G(d,p)	2.087	0.967	108.0	2.129	0.967	107.5

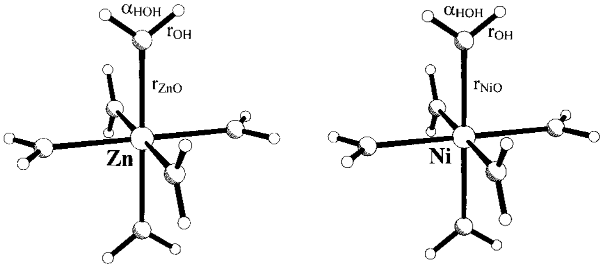

Figure 1. Computed equilibrium geometries of $[Me(H_2O)_6{}^{2+}]$ complexes (Me = Zn, Ni).

two parameters (r_{OH} and α_{HOH}) are almost invariant within the higher basis sets. We conclude that the B3LYP/6-311+G(d) level is sufficient for the very precise geometries of the transition metal complexes of similar type. The optimization of the transition metal complexes of comparable size is well within the power of the supercomputers. For example, one optimization step of the $[Ni(H_2O)_5(CH_3OH)]^{2+}$ molecule took about 6 h of CPU time on an SGI Power Challenge XL (R10000 processor) computer.

The optimized geometries of substituted species are depicted in Figure 2. It should be pointed out that the optimization procedure ended up in the minima corresponding to the octahedral arrangement of ligands around the central metal ion with the exception of the $[Ni(H_2O)_5(CH_3SH)]^{2+}$ complex, where methanethiol drifted apart and the molecule resembles the $[Ni(H_2O)_5]^{2+}$ complex in trigonal bipyramidal coordination with methanethiol weakly bound to the coordinated water molecules. However, it was not excluded from further calculations, as it enabled us to test the applicability of DFT for weakly bound systems with the functional group present in the second solvation layer and not directly coordinated to the metal. Some justification of the reliability of DFT methods for the description of hydrogen-bonded systems can be also found in the literature.[54]

The optimized metal−ligand bonds are about 2% longer for zinc complexes than for nickel ones. It corresponds to the ratio of nickel and zinc effective ionic radii (0.94).[55] The bond angles between the donor atom of ligated functional group and the water oxygens in the equatorial positions are distorted from "octahedral" 90° by approximately 5° as a result of nonbond interactions between the ligands. To further corroborate the computational results, we have searched the Cambridge Structural Database (version 5.12.)[56] for the small complexes of Zn^{2+} and Ni^{2+} having nitrogen, oxygen, and sulfur as donor atoms. The hexaaquazinc(II) and nickel (II) cations and several structures bearing similarity to the substituted molecules (such as hexaamminenickel(II) cation) were found in the database. The Ni−O (Zn−O) bond distance in the crystal of $[Ni(H_2O)_6]Y$ ($[Zn(H_2O)_6]Y$) is about 2.06 Å (2.09 Å), depending upon the anion. It agrees well with the computed value of 2.087 Å (2.129 Å). The average Ni−N bond distance in NH_3-containing complexes of nickel (II) is 2.10 Å (computed, 2.08 Å), Zn−O in $[Zn(CH_3OH)_2(X)_4]Y$ is 2.11 Å (computed, 2.08 Å), and Zn−S in $[Zn(CH_3SCH_3)(X)_5]Y$ is 2.52 Å (corresponding to 2.61 Å in $[Zn(CH_3SH)(H_2O)_5]Y$). It clearly shows the plausibility of the computed values. The small differences should be ascribed to crystal packing forces and to the fact that the compared molecules were not in many cases identical.

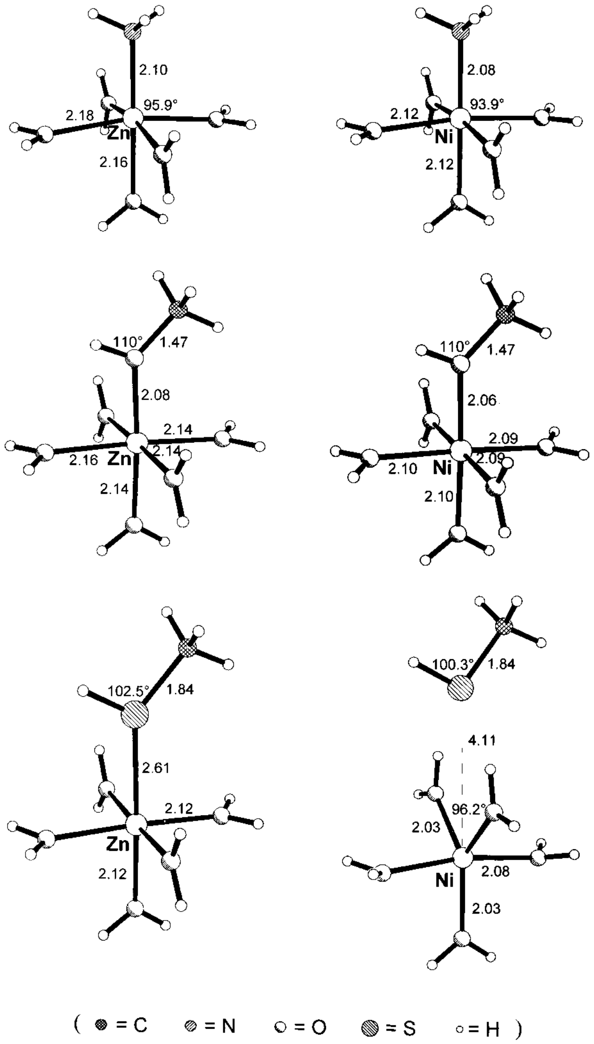

Figure 2. Equilibrium geometries of $[Me(H_2O)_5(Y)]^{2+}$ complexes (Me = Zn, Ni; Y= CH_3OH, NH_3, CH_3SH) computed at the B3LYP/6-311+G(d,p) level.

Reaction Energies. In a subsequent step, we have investigated the convergence of the value of the reaction energy of reaction 1 ($\Delta E = E_{products} - E_{reactants}$) with respect to the size of the basis set. Five different basis sets were applied. The

TABLE 2: Reaction Energies (in kcal mol^{-1}) Calculated with B3LYP Functional in Various Basis Sets for the Reaction 1[a]

	Ni			Zn		
basis set	CH_3OH	NH_3	CH_3SH	CH_3OH	NH_3	CH_3SH
DZP	−2.3	−9.3	26.5	−1.9	−11.7	4.3
DZ2P	−1.9	−8.4	27.2	−1.7	−18.0	4.3
6-311G(d,p)	−1.9	−7.1	18.1	−1.7	−6.2	6.8
6-311+G(d,p)	−3.5	−8.9	10.0	−3.4	−8.4	5.5
6-311++G(2d,2p)	−3.8	−9.3	8.5	−3.6	−8.9	4.3
6-311++G(2df,2pd)	−3.6	−9.0	8.6	−3.5	−8.6	4.4

[a] Negative values indicate that reaction proceeds from reactants to products.

TABLE 3: Comparison of Reaction Energies (in kcal mol^{-1}) for Reaction 1 Obtained with B3LYP, CCSD(T), and QCISD(T) Methods Using B3LYP/6-311+G(d,p) Optimized Geometries

method/basis set	Zn, NH_3	Zn, CH_3OH	Zn, CH_3SH	Ni, NH_3
B3LYP/6-311G(d)	−4.5	−0.1	15.4	−5.4
QCISD(T)/6-311G(d)	−4.4	−0.9	16.1	−4.9
CCSD(T)/6-311G(d)				−4.9
B3LYP/6-311+G(d,p)	−8.4	−3.4	5.5	−8.9
QCISD(T)/6-311+G(d,p)	−8.4			
B3LYP/6-311++G(2df,2pd)	−8.6	−3.5	4.4	−9.0

geometry was reoptimized in each basis set except for the last computation (B3LYP/6-311++G(2df,2pd)) where we used B3LYP/6-311+G(d,p) optimized geometry. The results are summarized in Table 2. It can be seen that the convergence of the reaction energies is excellent in 6-311+G(d,p) and higher basis sets.

In the last step, the relevance of the B3LYP limit (as obtained from the above-mentioned set of reaction energies) has been examined. Since we are not aware of any published experimental data concerning the energetics of such substitution reactions on the hydrated ions of Zn^{2+} and Ni^{2+}, several QCISD(T) calculations and one CCSD(T) calculation were performed on the B3LYP/6-311+G(d,p) optimized geometries. Three substitution reactions of hexaaquazinc (II) and one of nickel(II) cation were taken into account, as the calculations of this quality were extremely demanding and sometimes even beyond the capabilities of the Gaussian 94 program. The results are summarized in Table 3.

It can be seen that an excellent agreement between B3LYP and QCISD(T) sets of reaction energies (in given basis set) has been achieved. The mean absolute difference is 0.46 kcal mol^{-1}, and the maximum absolute difference is 0.84 kcal mol^{-1}. It is within the 2 kcal mol^{-1} range, which is generally accepted as the value of experimentally achievable accuracy.

TABLE 4: Interaction Energies (in kcal mol^{-1}, Defined by Eq 2) and Interatomic Metal−Ligand Distances (Å, in Parentheses) of Zn^{2+} Ion with NH_3, CH_3OH, CH_3SH with Respect to the Coordination Geometry of the Metal Ion, Calculated at the B3LYP/6-311++G(2df,2pd)//B3LYP/6-311+G(d) Level

		ligand			
coordination number	coordination geometry	H_2O	NH_3	CH_3OH	CH_3SH
6	octahedral	0.0	−10.7	−4.1	8.9
		(2.13)	(2.10)	(2.08)	(2.61)
4	tetrahedral	0.0	−17.8	−8.6	−7.3
		(2.00)	(2.04)	(1.97)	(2.39)
1	bare ion	0.0	−33.6	−25.6	−48.2
		(1.88)	(1.97)	(1.86)	(2.35)

Role of Coordination Geometry. For Zn^{2+} complexes, we have calculated the reaction energies of reaction 1 for $n = 1$, 4 (tetrahedral coordination), 6 (octahedral coordination) at the B3LYP/6-311++G(2df,2pd)//B3LYP/6-311+G(d) level. To compare directly the interaction energies of the zinc(II) cation in three different modes of coordination, a slightly different computational approach was used. First, we have optimized the molecular geometry and calculated the energy of the $[Me(H_2O)_{n-1}(Y)]^{2+}$ complex with the angles at the metal center fixed in the octahedral (tetrahedral) geometry. Subsequently, at the optimized geometry of the above complex, the metal was substituted for a ghost atom (i.e., only basis functions were left from metal center) and the energy of the $Bq(H_2O)_{n-1}(Y)$ system computed (Bq stands for ghost atom). Thus, we have excluded the nonbond interactions between ligands and estimated the BSSE error. The interaction energy of the metal with a functional group Y is defined as

$$E(Y)_{int} = E([Me(H_2O)_{n-1}(Y)]^{2+}) - E(Bq(H_2O)_{n-1}(Y)) - (E([Me(H_2O)_n]^{2+}) - E(Bq(H_2O)_n)) \quad (2)$$

The equilibrium geometries and interaction energies are summarized in Table 4.

The metal−ligand distances and interaction energies of the different functional groups are strongly dependent on the coordination geometry of the central metal. It is most profound in the case of methanethiol. It is the least favorable ligand for Zn^{2+} in an octahedral arrangement. However, it should be capable of replacing a water molecule in the model $[Zn(H_2O)_4]^{2+}$ molecule and it should exhibit the highest affinity for bare Zn^{2+}. We presume that it is the result of the highest polarizibility of sulfur in methanethiol (compared to nitrogen in NH_3 and oxygen in H_2O, CH_3OH). The magnitude of this effect is largest for the bare ion because of the highest effective charge on the metal and the shortest interatomic distance.

The dependence of the interaction energy on the coordination environment should be kept in mind when calculating the affinities of different functional groups for the transition metal ion. When the transition metal centers are modeled, it is erroneous to use the interaction energies calculated for the bare ions or different coordination geometry.

The computed interaction energies in octahedral arrangement (which is the coordination mode of nickel(II) and zinc(II) in aqueous solution) agree with the qualitative HSAB (hard-and-soft acids and bases) theory of Parr and Pearson,[57] often used in the coordination chemistry. According to it, Zn^{2+} and Ni^{2+} should exhibit a higher tendency to bind nitrogen- or oxygen-containing donors rather than a sulfhydryl group. The calculations showed that the most favorable ligand for both zinc(II) and nickel(II) cations is ammonia followed by methanol. On the other hand, methanethiol should not be capable of replacing a water molecule from the metal coordination sphere. This tendency is more profound in the case of the $[Ni(H_2O)_5(CH_3SH)]^{2+}$ complex, which has been discussed above.

Conclusions

In this article, we attempted to present the methodology that can be used for the computations of accurate interaction energies of different functional groups with transition metal ions. We have studied the convergence of the molecular geometry and reaction energy with increasing size of the basis set. The results have been compared with the structural data from Cambridge Structural Database and with the reaction energies obtained from

QCISD(T) calculations. The important question of the influence of coordination geometry of metal on the interaction energy has been addressed.

From the results listed in the previous section it can be concluded that DFT/B3LYP (both restricted and unrestricted) is a reliable method for transition metal complexes of ionic character with the molecular ground electronic state described by a single determinant. The single vs multireference character of wave function is not always a trivial problem that can be decided a priori, and therefore, CAS SCF calculation (at least on model compounds) should precede. It should be followed by the optimization using a medium basis set (6-311+G(d)) and the energy recomputed with a large basis set (6-311++G(2df,2pd)). The reaction energies for the substitution reactions of transition metal ions, computed according to the above scheme, were shown to differ by about 0.5 kcal mol^{-1} from the reference QCISD(T) values, what we consider to be an excellent agreement. As a reminder, B3LYP is several orders less demanding than coupled cluster or quadratic configuration interaction method.

It has been shown that the interactions of different functional groups with transition metals are very sensitive to the coordination geometry of a metal. It is therefore necessary to compute the interaction energies in the target coordination environment.

The calculations on model compounds containing the transition metals can help to improve their parameters in force fields, explain the different stability of individual stereoisomers of transition metal complexes, and give some hints about the nature of the effects governing the selectivity of certain compounds for a particular transition metal. There are still many problems to be solved, and every step toward efficiency and accuracy is important.

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