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Characterization of the Zn^{q+}-imidazole (q = 0, 1, 2) organometallic complexes: DFTs vs. standard and explicitly correlated post Hartree-Fock methods

K. Boussouf,[a, b] R. Boulmene,[a, b] M. Prakash,[a, c] N. Komiha,[b] M. Taleb,[d] M. Mogren Al-Mogren,[e] M. Hochlaf [*,a]

[a)] Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France

[b)] LS3ME-Equipe de Chimie Théorique et Modélisation, Université Mohamed, Faculté des Sciences Rabat, Maroc

[c)] Institut Charles Gerhardt Montpellier, UMR 5253 CNRS UM2 ENSCM UM1, Université Montpellier 2, Place E. Bataillon, Montpellier cedex 05, 34095, France

[d)] Laboratoire LIMME, Université Sidi Med Ben Abdellah, Fac des Sciences Dhar El Mehrez, Fès, Maroc

[e)] Chemistry Department, Faculty of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Kingdom of Saudi Arabia

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*Author for correspondence: M. Hochlaf: Phone: +33 1 60 95 73 19. Fax: +33 1 60 95 73 20. Email: hochlaf@univ-mlv.fr

Abstract

At present, we investigate the bonding, the structures, the stability and the spectroscopy of the $Zn^{q+}Im$ (where q = 0, 1, and 2) complexes, which are zeolitic imidazolate frameworks (ZIFs) and Zn-enzymes sub-units. Through a benchmark work, we used density functional theory (DFT) with dispersion correction and standard and explicitly correlated *ab initio* methods. For neutral Zn^0Im, we found two stable weakly bound forms: (i) a stacked ferrocene-like complex; and (ii) a planar σ-type complex. This is the first report for Zn^0 organic compound of stacked ferrocene structure. The most stable isomers of the ionic species consist on σ-type bonded complexes. The roles of various types of covalent and noncovalent interactions within these complexes are discussed after vibrational, NBO, charges and orbital analyses. For neutrals, van der Waals (vdWs) and charge transfer through covalent as well as noncovalent interactions are in action; whereas the bonding is dominated by charge transfer from Zn to Im within the ionic species. These findings are important to understand, at the microscopic level, the structure and the bonding within the ZIFs and the Zn-enzymes. Moreover, we establish the ability and reliability of M05-2X and PBE0 functionals for the simultaneous correct description of covalent and noncovalent interactions since this DFT leads to close agreement with post Hartree-Fock methods. The newly launched M11 functional is also suited for the description of noncovalent interactions. Therefore, M05-2X and PBE0 functionals are recommended for studying the larger complexes formed by Zn and Im, such as the ZIFs and Zn-enzymes.

I. Introduction

Complexes between imidazole (Im) or Im derivatives and transition metal play crucial roles in chemical, biological and industrial domains.[1,2,3,4] In biological media, Im and imidazolate act as natural ligands of Zn^{2+} cation and their complexes are involved in important biological processes: They constitute the main part of the active sites of some metalloenzymes (e.g. angiotensin-converting enzyme, thermolysin, hydrolases, isomerizes, lyase, ligases and carbonic anhydrase [5,6,7,8]), where Im is an essential cofactor and Zn^{2+} ion is directly involved in catalytic mechanisms.[9,10] Specifically, carbonic anhydrase, which main function is to hydrolyze CO_2, is involved in many fundamental physiological processes such as respiration, photosynthesis or acid-base balance of all living organisms.[11,12] From an industrial and environmental point of view, Im moiety is the predominant organic part in most of zeolitic imidazolate frameworks (ZIFs) where it is linked to a Zn^{2+} ion. The total charge of the system is neutral in bulk phase. The Zn-Im complexes represent hence sub-units of ZIFs. The structural backbone of ZIFs is constructed from tetrahedral units formed by one bivalent metal ion ($M^{2+} = Zn^{2+}/Co^{2+}$) and four imidazolate anions. Such compounds present a well-established structural topology with a large structural diversity. They exhibit a high porosity which is potentially used for gas storage and separation techniques.[13,14,15] Several studies treated the macroscopic properties of ZIF material with gas molecules such as H_2, N_2, CH_4 and CO_2 and mixtures of those molecules.[16,17,18,19,20,21,22,23] These reports explained that gas molecules are adsorbed on the linker part of ZIFs, whereas information on the roles of transition metal ion and its interaction with the organic part are scare. The microscopic properties of these kinds of complexes are still unclear. The characterization of the interaction within the Zn-Im complexes is crucial for controlling and modulating the potential gas capture / sequestration ability of ZIFs and the metalloenzyme's activity.

Molecular modeling studies have played significant role in providing reliable information on molecular systems. Eventually, density functional theory (DFT) and *ab initio* methods (e.g. Møller-Plesset second order perturbation (MP2)[24]) complement each other to investigate medium and large sized organometallic complexes. In this context, previous theoretical studies showed that earlier DFTs (e.g. B3LYP) are well suited for the accurate description of strongly bonded and electrostatic interactions.[25-28] For instance, Piquemal *et al.*[26] have used various *ab initio* (MP2) and DFTs (PW91, B3PW91, BLYP, and B3LYP) methods with DZVP2 basis set to predict the intermolecular interaction energy for a series of dimers including the most stable form of the Zn^{2+}Im complex, which is confirmed by the most recent high-level *ab initio* benchmark studies of Rayon *et al.*[27] Also these authors determined the mean signed error (MSE) and standard deviation (SD) of Zn(II) complexes BEs at the DFT-B3LYP and DFT-TPSS with optimum (Pople's) and aug-cc-pVTZ (aVTZ) basis sets. In addition, Piquemal *et al.* and Rayon *et al.* used SAPT (Symmetry Adapted Perturbation Theory) methodology giving hence insights into the contributions of induction, electrostatics, exchange, and dispersion on the binding energies of ionic Zn^{2+}Im. For weak 3d transition metal containing complexes, these DFTs relatively fail in predicting their thermochemical properties.[28] Difficulties reside on the accurate and simultaneous description of the covalent / noncovalent bonds within the organic part and the Zn-N (Im) organo-metal bond. The nature of this organo-metal bond is still unclear. Recently, Wilson and coworkers[29] established the performances of generalized gradient approximation (GGA), *meta* and *hybrid* GGA functional in connection with cc-pVTZ to cc-pVQZ basis sets for such studies.

In the present contribution, we perform systematic investigations of the Zn^{q+}Im (q = 0, 1, 2) complexes using various DFTs (with and without inclusion of D3 dispersion) and wavefunction based *ab initio* methods to deduce the stable forms and to characterize the nature of the bonding between Zn and Im. Moreover, we carried out computations using the recently implemented explicitly correlated Møller-Plesset ((R)MP2-F12) and coupled clusters ((R)CCSD(T)-F12) approaches, which account for electron correlation with reduced computational cost. After benchmarks, we discuss the reliability of DFTs and various corrections (e.g. BSSE, D3) for the accurate description of this organo-metallic compound. A generalization to larger organometallic compounds is also proposed.

II. Computational Details

Functional groups containing nitrogen atoms binding directly to bivalent Zn cation have been thoroughly studied using various DFTs.[30,31,32] Based on these studies and several benchmarks,[33,34] we have selected a set of GGA, exchange correlation density functionals and hybrid meta-GGA (Truhlar's M05-2X, and M11 functional)[35] along with the 6-311++G(d,p) basis set to deduce the equilibrium structures, the energetics, the spectroscopy, the chemical bonding (covalent, charge transfer and van der Waals (vdWs) types) and the role of dispersion in the stability of Zn^{q+}Im (q = 0, 1, 2) complexes. Our computations were carried out using PBE [36], PBE0 [37], M05-2X with and without inclusion of Grimme's [38] (DFT-D3) dispersion correction as implemented in GAUSSIAN 09 and (*G09-D.01*). [39] In addition, M11 functional was employed for the optimization of the equilibrium structures (with integral = ultrafine keyword). The geometry optimizations were performed either with or without consideration of basis set superposition error (BSSE) and counterpoise (CP) correction for comparison. The SCF=XQC keyword was used in SCF convergence. Several initial configurations were used as starting point for these optimizations. To assess on the nature (minimum or transition state) of the computed stationary points, frequency calculations were carried out using the PBE, PBE0, M05-2X functionals in connection with the 6-311++G(d,p) basis set. All geometrical parameters were relaxed. Anharmonic frequencies were deduced after scaling the harmonic ones (scaling factor 0.9417).[40] Only stable structures on the lowest potential energy surface of the corresponding complexes are quoted and discussed below.

Further computations on the stable forms found using DFT were done at the (R)MP2,[41] spin-component scaled MP2 (SCS-MP2)[42] and coupled cluster approach in the singles and doubles approximation with a perturbative treatment of the triple excitations [43] ((R)CCSD(T)) levels. Frequency computations were also performed using the (R)MP2 method with the 6-311++G(d,p) or aug-cc-pVDZ basis sets. We took also advantage of the newly implemented explicitly correlated MP2, i.e. (R)MP2-F12,[44] and coupled cluster, i.e. (R)CCSD(T)-F12 [45] approaches to deduce accurate energetics and to attest on the reliability of DFTs for accurate description of the organometallic bond within these complexes. Here, valence electrons were active and the core electrons were frozen and there were no scaling for perturbative triples for (R)CCSD(T)-F12. For these computations, the C, N, O and H atoms were described using the aug-cc-pVXZ (aVXZ, where X = D, T) Dunning and co-workers' basis sets [46] as atomic orbitals, which were complemented by the corresponding resolution of the identity (RI) basis set and for the density fitting for explicitly correlated computations. For Zn, we used either Dunning and co-workers basis sets' or the recently launched aVTZ(-PP)[47] and the corresponding pseudopotential-based OPTRI auxiliary (OptRI) correlation consistent polarized basis set [48] and auxiliary MP2FIT correlation consistent polarized basis sets.[49] For these computations we used the MOLPRO (Version 2012.1) package. [50] Further details on the methodology used here can be found in Refs. [51]

III. Results and discussion

a. Optimized equilibrium structures

The optimized geometries of Zn^{q+}I*m* (q = 0, 1, 2) complexes along with the main geometrical parameters computed using PBE, PBE+D3, PBE0, PBE0+D3, M05-2X, M05-2X+D3, M11, (R)MP2, (R)CCSD(T), (R)MP2-F12 and (R)CCSD(T)-F12 methods are given in Figure 1 and Table 1. The full set of the harmonic frequencies of these complexes is given in Table S2 of the Supplementary material. This Table shows that all levels of theory agrees on the nature of the stationary point except PBE, which provided a transition state for Zn^0Im I instead of a minimal structure. This makes questionable the use of PBE for neutral weakly bound organo metallic complexes.

Our calculations show that Im possesses close equilibrium structure in Zn^{q+}Im (q = 0, 1, 2) complexes and in isolated Im. This is independently on the theoretical method used for optimization. This was recently point out also for Im either isolated or adsorbed at gold clusters.[52] Whereas the Zn-Im intermonomer bond strongly changes upon ionization and it shows some deviations depending on the theoretical methodology used for computations. For neutral complexes between Zn^0 and Im, two stable forms were found. Hereafter, they are denoted as Zn^0Im I and Zn^0Im II. In contrast, a unique planar structure is found for the ionic forms ($Zn^{+1}Im$ and $Zn^{2+}Im$). Zn^0Im I, $Zn^{+1}Im$ and $Zn^{2+}Im$ are analogous to the ZIFs environment. Zn^0Im II is ferrocene like complex. $Zn^{2+}Im$ was already identified in the work of Piquemal *et a.l*[26] and of Rayon *et al.*[27] For Zn^{2+} -- benzene, Rayon *et al*. found a ferrocene like structure as the one we have for Zn^0Im II, which is the first neutral Zn-organic compound for such structure.

Zn^0Im I is planar where the Zn is linked to the unprotonated nitrogen of Im. The Zn-N bond within this complex is dominated by partially covalent interaction between Zn and N (see below). Using all methods, the Zn-Im distance (denoted as R_{ZnN}, Table 1) is computed in the range 2.9 – 3.2 Å. The PBE0 and M11 computed distances are in excellent agreement with the relatively costly post Hartree-Fock methods (both standard and explicitly correlated ones). In addition, Table 1 shows that the increase of the size of the basis set or the accounting for large amounts of electron correlation tend to lengthen this distance. For instance, R_{ZnN} is computed 2.962 Å and 3.022 Å using MP2/aVDZ and MP2/aVTZ, respectively. The MP2-F12/aVTZ(-PP) R_{ZnN} distance is close to the MP2/aVTZ one. This distance turns out to be 3.058 Å at CCSD(T)/aVDZ i.e. close enough the MP2/aVTZ(-PP) value. This attests on the good quality of the aVTZ(-PP) basis set recently launched by Peterson and co-workers. For this isomer, Table I shows also that full inclusion of D3 and BSSE corrections within PBE, PBE0 and M05-2X computations leads to sensitively similar values as those obtained without considering these corrections, especially for the Im monomer.

Zn^0Im II is a ferrocene like structure. The interaction between Zn and Im is mainly of vdWs type, where the π^* molecular orbital (MO) of Im interacts with the 4s vacant atomic orbital (AO) of Zn (Figure 2). Because of its weakly bond nature, the Zn-Im distance (denoted as $R_{Zn-\pi}$) represents a critical test for DFTs, basis sets and *ab initio* techniques to be used for computations of larger sized organo-metallic compounds. Table 1 shows that $R_{Zn-\pi}$ length decreases from 3.337 (2.938) Å to 3.284 (2.896) Å to 3.215 (2.755) Å when using PBE, PBE0 and M05-2X DFTs with (without) D3 correction. In contrast to Zn^0Im II complex, solely the M05-2X and M11 values are in close agreement with the MP2 distance (of 2.704 Å) computed with the same basis set. An overestimation is observed with the other DFTs in contrast to the results obtained using post Hartree-Fock methods (Table 1). For instance, using the aVXZ and aVXZ(-PP) basis sets and the MP2, MP2-F12 or CCSD(T) techniques, we compute $R_{Zn-\pi}$ of 2.6 – 2.7 Å in close agreement with the M05-2X and M11 values. These findings are online with the main conclusions of our recent benchmark studies on the CO_2 interaction with isolated Im or with Im adsorbed on gold surface or clusters, where we established the robustness of M05-2X DFT for the accurate description of σ type H-bond and π stacking interactions in gas and gas-surface media.[34]

For Zn^{+1} and Zn^{+2} metallic ions interacting with Im, a planar form with a relatively strong covalent bond are found as global minima. Here, Zn is linked to the unprotonated nitrogen. The Zn-Im distance (R_{ZnN}) shortens upon ionization. Indeed, it is ~ 2 Å in Zn^{+1}Im and ~1.85 Å in Zn^{+2}Im. The Zn-N distance in Zn^{+2}Im agrees well with earlier reports.[27] When comparing the values computed using various methods and basis sets (Table 1), similar trends as discussed above for Zn^{0}Im I and Zn^{0}Im II can be drawn. Incorporation of D3 correction slightly enhances this distance due to the dispersive character between Zn and N atom's.

For neutral species, it can be found from our calculations that the predicted intermonomer distances using DFT+D3 are significantly larger than their values obtained only the respective DFT. Particularly the highly dispersive nature of Zn^{0}Im II structure is affected by D3 correction when compare with gold standard CCSD(T). Whereas bonding nature between Zn and N at all other complexes predicted by DFT's are in very good agreement with the high level *ab initio* methods. This was recently pointed out by Schluns *et al.,*[53] who clearly stated that the calculated interaction energy for weakly bound systems from subsystem-DFT method is superior to the well-known KS-DFT results without dispersion correction. Once again we can conclude, computationally low cost hybrid functionals are suited for the large size metal organic and organometallic complexes.

b. Binding energies

Apart from geometries, binding energies (BEs) of the complexes are very important to validate suitable DFTs for the accurate and simultaneous description of both covalent and noncovalent interactions. At present, BEs were calculated using within the supermolecule approach and corrected for basis set superposition error (BSSE) using the counterpoise (CP) procedure as suggested by Boys and Bernardi [54]

$$BE = \left(E_{AB} - \left(E_{A} + E_{B}\right)\right)$$

where E_{AB} is the total energy of the Zn^{q+}Im (q = 0, 1, 2) complexes at equilibrium, E_{A} is the energy of the Zn^{q+} ion and E_{B} is the energy of Im at equilibrium.

Table 2 presents the BSSE corrected BEs for the Zn^{q+}Im (q = 0, 1, 2) complexes computed using PBE(+D3), PBE0(+D3), M05-2X(+D3), M11, (R)MP2, SCS-MP2, (R)CCSD, (R)CCSD(T), (R)MP2-F12, (R)CCSD-F12 and (R)CCSD(T)-F12 methods. For neutral species, all methods except PBE and M11 concord to establish that Zn^{0}Im II as the most stable form. The inclusion of D3 dispersion (i.e. PBE+D3) corrects this discrepancy. At the M05-2X+D3/6-311++G(d,p) level, we compute BE(Zn^{0}Im II) to be -2.45 kcal/mol and BE(Zn^{0}Im I) to be -1.48 kcal/mol. SCS-MP2 computations in connection with the aVTZ basis set lead to BE(Zn^0Im II) = -1.99 kcal/mol and BE(Zn^0Im I) = -1.07 kcal/mol. The MP2-F12 explicitly correlated values are close to those deduced using standard MP2 (cf. Table 2). Using the costly standard coupled cluster computations, we obtained BE(Zn^0Im II) = -2.49 kcal/mol and BE(Zn^0Im I) = -1.63 kcal/mol, which are close to the corresponding explicitly correlated values, whereas the computational cost of the latter calculations is reduced by two orders of magnitude (both CPU and disk occupancy). Similar trends can be given for the results on the ionic species. For Zn^{+1}Im, our BE is about ten times larger than the one measured by two-color resonant photoionization of a ZnAr metastable state where only vdWs forces are in action.[55] This confirms the occurrence of a covalent bond in our case between Zn^{+1} and Im. For Zn^{+2}Im, we compute a BE of ~ -180 kcal/mol. This BE agrees with the B3LYP/aVDZ (& cc-pVTZ) BE (of ~ -182 (& -183) kcal/mol) computed by Dopfer and coworkers.[56] Such agreement is not surprising for the Zn^{2+}Im species because of the "relatively strong" nature of its Zn-Im bond, which is correctly accounted for by B3LYP. Rayon *et al.*[27] have employed SAPT approach to predict a BE of ~ -179.5 kcal/mol for Zn^{+2}Im complex, which is in excellent agreement with our results.

More generally, the examination of Table 2 shows that the aVDZ is not diffuse enough to lead to accurate BEs, whereas both aVTZ and aVTZ(-PP) remediate to this deficiency. Furthermore, both aVTZ and aVTZ(-PP) provide close results, whereas the cost of these computations is reduced with the later basis set. Hence, the aVTZ(-PP) basis set should be enough for the accurate description of organometallic species. In addition, it worth noting that explicitly correlated methods lead to BEs close to their values obtained using the corresponding standard methodologies, whereas the cost of such computations is strongly reduced using the explicitly correlated ones. Finally, we suspect that the triple contribution within the coupled cluster calculations may overestimate these BEs, especially for the neutral species. The origins of this effect are unclear. This may be related to the nature of the bonding within these complexes.

Our computations reveal that in despite that PBE and PBE0 DFTs provide BEs close to post Hartee-Fock *ab initio* methods, the inclusion of D3 correction (i.e. PBE+D3 or PBE0+D3) leads to an overestimation of the corresponding BEs especially for the Zn^0Im neutral weakly bound complexes. In contrast, both M05-2X and M05-2X+D3 values fall into those computed by higher levels. The other newly developed M11 functional underestimates the BEs of Zn-Im covalent bonded complex. A systematic study on the Zn-Rg (Rg= rare gas)[57] is also online with these findings (see Table S1 of the Supplementary material). This joins the well-established performance and suitability of M05-2X for the accurate description of both π and σ types weak interactions.[34,58] Especially, our systematic study shows that previous BEs of organo-metallic compounds should be reevaluated using the M05-2X+D3 or the MP2-F12 or the CCSD(T)-F12 approaches for better accuracy. This is crucial for the precise deduction of the thermochemical data of these species. Such accurate data are also needed to be incorporated into dynamical computations of the macromolecular properties of ZIFs and Zn-enzymes.

c. On the bonding within the $Zn^{q+}Im$ (q = 0, 1, 2) complexes

The BEs order is $Zn^{+2}Im$ > $Zn^{+1}Im$ > $Zn^{0}Im$. To quantify the nature of intermolecular interactions, the charge transfer between Im and Zn complexes, NBO[59] and frontier MOs shape analyses were carried out at the M05-2X/6-311++G(d,p) level of theory. The various kinds of donor-acceptor interactions favor the stability of these complexes.

We display in Figure 2 the isosurface density (0.02 a.u) plots of neutral and ionic $Zn^{q+}Im$ complexes calculated at the M05-2X optimized geometries. This figure shows that the HOMOs of $Zn^{0}Im$ I and of $Zn^{+1}Im$ result from the overlap between the 4s AO of Zn and the lone pair of the unprotonated nitrogen of Im. Whereas, the bonding in $Zn^{0}Im$ II is due to the interaction of the Zn 4s AO with the outermost π* MO of Im. For LUMO-LUMO+2, they consist mostly on interactions between either the lone pair or the outermost π* of Im and the 4p AOs of Zn. The 4s and 4p AOs are Rydberg. They are hence diffuse in nature. Therefore, only large basis sets and methodologies, which take into account of such effects, are valid. This agrees well with the better data obtained using the larger aVTZ basis set compared to those obtained with aVDZ.

The strength of the donor-acceptor interaction between the occupied orbital of the donor (ϕ_i) and the unoccupied orbital of the acceptor (ϕ_j) can be approximated by the second order perturbation expression:

$$E_2 = \Delta E_{ij}^{(2)} = 2\frac{\left\langle \phi_i \middle| \hat{F} \middle| \phi_j \right\rangle^2}{\varepsilon_j - \varepsilon_i}$$

Where ε_i and ε_j are NBO energies, $F_{ij} = \left\langle \phi_i \middle| \hat{F} \middle| \phi_j \right\rangle$ is the Fock matrix element. The existence of donor-acceptor interactions in these complexes are evident from the second order perturbation energy ($E_{ij}^{(2)}$) values.

The NBO analyses of all complexes are provided in Table 3. This table shows that donor-acceptor interactions within these complexes mainly involve the lone pairs of the unprotonated nitrogen atom (LP(1)N1) of Im and Zn metal along with intra molecular charge transfer to the Im aromatic ring. The NBO E_2 values for $Zn^{0}Im$ I and $Zn^{0}Im$ II are 2.26 and 0.35 kcal/mol, respectively. This clearly reveals that charge transfer in Zn^0Im I is more favorable than in Zn^0Im II. This is due to the perfect orbital overlapping between Zn and Im(N1) in Zn^0Im I, in contrast to Zn^0Im II where the interactions are due mostly to dispersion (see Figure 2 and Figure 1 for the corresponding numbering of the atoms). In addition, intramolecular charge transfer within the Im moiety stabilizes these complexes. For example, the lone pair of protonated nitrogen (LP(1)N5) interacts with C-C and C-N bonds of Im where charge transfer through the C-N bond is more predominant than the C-C bond. The respective E2 value for Zn^0Im I (Zn^0Im II) is ~65 (63) and ~42 (43) kcal/mol. One more significant charge transfer is also observed from protonated nitrogen (LP(1)N5) to RY*(2) C4 carbon atom. For neutral complexes, the respective E2 values are ~4 kcal/mol.

For $Zn^{+1}Im$, the charge transfer from LP(1)N1 to Zn is 1.41 and from LP(1)N1 to RY*(C2) is 2.63. For $Zn^{+2}Im$, the corresponding values are 4.89 from LP(1)N1 to Zn and 5.64 from LP(1)N1 to RY*(C2). All values are in kcal/mol. For both complexes, acidic carbon atom (C2) is involved in the charge transfer whereas the main contribution comes from the C4 carbon for neutrals. This clearly reveals that charge transfer pathways for neutral and charged systems are very different and that they contribute significantly in different ways for the stability of the complexes as well as. These values are in excellent agreement with the calculated geometrical distances and BEs. Also, these findings agree quite well with those deduced by Dopfer and co-workers[56] after comparison of the structural and vibrational properties of the imidazole cation and of $Zn^{2+}Im$. These authors showed indeed that ligand-metal interactions are dominated by σ donation, whereas contributions from π donation should be minor.

d. Vibrational spectroscopy

For the low frequency modes of $Zn^{q+}Im$ (q = 0, 1, 2) complexes, Table 4 lists their harmonic wavenumbers, their assignment based on a normal mode analysis and their IR intensities. These modes are related to the vdWs vibrations within these complexes. We considered hence three intermonomer modes: the stretching, the bending and the oscillating vibrations. These values once measured represent a critical test of the theoretical methodologies used here and devoted for the description of weakly bound organometallic clusters. The full set of harmonic frequencies is given in Table S2 of the supplementary material.

The calculated scaled vibrational stretching frequencies, intensities and respective shifts of Im and $Zn^{q+}Im$ complexes are given in Table 5. The calculated ν_{NH} and ν_{CH} frequencies for Im are 3518 and 3103 cm^{-1}, respectively. These values are close to the corresponding experimental values. The complexation induced shifts were calculated for the asymmetric (ν_{as}) and symmetric (ν_{ss}) stretching frequencies of N-H and C-H of isolated Im. Upon complexation, the ν_{CH} frequencies of Zn^0Im I and

Zn^0Im II red shift as well as ν_{NH} in Zn^0Im I. In contrast, ν_{NH} remains almost unchanged in Zn^0Im II. This is confirming one of the highly dispersive model complex with metal and aromatic environment. For ionic clusters, the calculated red shift values are relatively large. For $Zn^{+1}Im$ and $Zn^{+2}Im$, the ν_{NH} are lowered by 53 and 127 cm^{-1}, respectively. Generally, the calculated ν_{CH} frequencies are blue shifted in most of the $Zn^{q+}I$*m* complexes. The effects on the C-H stretching band intensities are less pronounced.

IV. Conclusions

The structure, stability and low frequency vibrational spectra of $Zn^{q+}Im$ (q = 0, 1, 2) complexes were treated using various DFTs with and without inclusion of D3 dispersion correction. Møller-Plesset (MP2), SCS-MP2, MP2-F12, standard and explicitly correlated coupled clusters additional computations were carried out to benchmark suitable DFT for the treatment of larger organometallic compounds. Our study establishes the ability and reliability of M05-2X(+D3) functional for the accurate description of covalent and noncovalent interactions between Zn^{q+} and Im since it leads to close agreement with the large ab initio techniques. PBE0 and M11 may be used also for that purposes.

This work provides valuable information about the role of charge transfer and vdWs interactions within the $Zn^{q+}Im$ complexes. This is important for the understanding of the biological, environmental and catalytic chemical related activities of these entities. We show that these effects may be probed using FAR-IR or IR spectroscopies.

From a perspective point of view, our work gives some insights for the investigation of new charge transfer complexes for various applications complementing, for instance, those pointed out recently by Terenzi et al.[60] Moreover, the present findings can be used for the derivation of accurate force fields for metalloproteins [61] or ZIFs.

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Table 1 Main geometrical parameters of $Zn^{q+}Im$ (q = 0, 1, 2) complexes computed at different levels of theory. For DFT computations, we give also those obtained including BSSE with D3 corrections during the optimizations. See Figure 1 for the definition of these parameters. Distances are in Å.

Basis set		6-311++G(d,p)								aVDZ		aVTZ(-PP)	aVTZ(-PP)	aVTZ
Method		PBE	PBE +D3	PBE0	PBE0 +D3	M05-2X	M05-2X +D3	M11	(R)MP2	(R)MP2	(R)CCSD(T)	(R)MP2-F12	(R)MP2	(R)MP2
Zn^0Im I	R_{NH}	1.016	1.015	1.006	1.006	1.004	1.004	1.009	1.010	1.013	1.013	1.005	1.006	1.006
	R_{CH}	1.087	1.087	1.081	1.081	1.078	1.077	1.084	1.081	1.088	1.091	1.076	1.077	1.077
	R_{ZnN}	3.041	2.915	3.091	2.935	3.211	3.198	3.107	3.094	2.962	3.058	3.024	3.061	3.022
Zn^0Im II	R_{NH}	1.016	1.015	1.006	1.006	1.004	1.004	1.009	1.010	1.014	1.013	1.006	1.007	1.007
	R_{CH}	1.087	1.087	1.080	1.081	1.077	1.077	1.084	1.081	1.087	1.090	1.077	1.077	1.077
	$R_{Zn-\pi}$	2.938	3.337	2.896	3.284	2.755	3.215	2.711	2.704	2.587	2.718	2.727	2.618	2.618
$Zn^{+1}Im$	R_{NH}	1.019	1.019	1.011	1.011	1.009	1.009	1.031	1.014	1.017	1.017	1.010	1.010	1.010
	R_{CH}	1.086	1.086	1.080	1.079	1.077	1.076	1.082	1.080	1.086	1.089	1.076	1.076	1.076
	R_{ZnN}	2.023	2.035	2.009	2.019	2.022	2.028	2.039	1.995	1.985	1.99	1.959	1.962	1.979
$Zn^{+2}Im$	R_{NH}	1.026	1.027	1.017	1.017	1.016	1.015	1.021	1.021	1.024	1.023	1.017	1.017	1.017
	R_{CH}	1.088	1.088	1.081	1.081	1.078	1.078	1.084	1.082	1.088	1.091	1.077	1.078	1.078
	R_{ZnN}	1.884	1.923	1.869	1.872	1.882	1.886	1.881	1.836	1.858	1.870	1.830	1.836	1.854

Table 2 BSSE corrected binding energies (BEs, kcal/mol^{-1}) of Zn^{q+}Im (q = 0, 1, 2) complexes computed at different levels of theories. D3 is when dispersion is included with DFT methods.

Basis sets		6-311++G(d,p)							aVDZ				aVTZ				aVTZ(-PP)					
Methods	PBE	PBE +D3	PBE0	PBE0 +D3	M05-2X	M05-2X+D3	M11	MP2	MP2	SCS-MP2	CCSD	CCSD(T)	MP2	SCS-MP2	CCSD*	CCSD(T)*	MP2	MP2-F12	CCSD*	CCSD(T)*	CCSD -F12*	CCSD(T) -F12*
Zn^{0}Im I	-1.28	-2.52	-1.10	-2.32	-1.28	-1.48	-2.51	-1.25	-1.60	-0.93	-0.64	-1.12	-1.76	-1.07	-1.06	-1.63	-1.69	-1.96	-1.07	-1.63	-1.90	-3.64
Zn^{0}Im II	-0.9	-2.80	-1.10	-2.90	-2.19	-2.45	-2.42	-2.16	-3.07	-1.76	-0.79	-1.81	-3.36	-1.99	-1.51	-2.49	-3.38	-3.78	-1.37	-2.45	-2.21	-4.39
Zn^{+1}Im	-67.0	-68.70	-62.8	-66.30	-66.00	-66.12	-59.74	-70.28	-62.78	-	-62.09	-62.93	-64.11	-	-64.26	-65.33	-65.61	-67.01	- 65.85	-67.49	-74.55	-75.8
Zn^{+2}Im	-192.9	-194.6	-162.5	-184.04	-177.9	-177.97	-171.3	-170.7	-174.0	-171.5	-172.4	-173.7	-176.2	-173.4	-175.14	-176.81	-182.4	-184.2	-180.6	-182.6	-181.1	-183.1

Table 3 Second-order perturbation analysis of the interaction between electron donor and acceptor orbitals in NBO basis calculated at the M05-2X/6-311++G(d,p) Level [a]

Complexes	**$\O_i$- $\O_j$**		**E_2 kcal/mol^{-1}**	**ΔE_{ij} a.u**	**F_{ij} a.u**	**Description of Charge Transfer (Inter/Intra)**
Zn^0Im I	LP(1) N1	LP*(7) Zn 1	2.26	0.59	0.033	Im → Zn
	LP(1) N5	BD*(2) C3 - C4	41.65	0.39	0.117	
	LP(1) N5	BD*(2) C2 - N1	64.65	0.37	0.139	Im →Im
	LP(1) N5	RY*(2) C4	**3.99**	1.12	**0.067**	Im →Im
Zn^0Im II	LP (1) N1	LP*(9) Zn 1	0.35	0.83	0.015	Im → Zn Im →Im Im →Im
	LP (1) N5	BD*(2) C2 - N10	63.27	0.37	0.138	
	LP (1) N5	BD*(2) C3 - C4	42.50	0.38	0.1	
	LP (1) N5	RY*(2) C4	**3.98**	1.13	0.067	
Zn^{+1}Im	LP (1)N1	LP*(6) Zn 1	1.41	0.37	0.034	Im → Zn Im →Im Im →Im
	LP (1)N1	BD*(2) C2 - N5	68.78	0.25	0.167	
	LP (1)N1	BD*(2) C3 - C4	20.94	0.35	0.118	
	LP (1) N1	RY*(4) C2	2.63	1.34	0.088	
Zn^{+2}Im	LP (1)N1	LP*(6) Zn 1	4.89	0.45	0.047	Im → Zn Im →Im Im →Im
	LP (1)N1	BD*(2) C2 - N5	87.70	0.33	0.152	
	LP (1)N1	BD*(2) C3 - C4	30.67	0.42	0.108	
	LP (1) N1	RY*(4) C2	5.32	1.28	0.083	

[a] The calculated second order perturbation energies (E_2 = in kcal/mol^{-1}),and F_{ij} is the Fock matrix element(in a. u.). BD for 2-center bond, BD* is for 2-center antibond, LP for 1-center valence lone pair and RY* for 1-center Rydberg. Numbering of atoms is shown in Fig. 1.

Table 4 Assignment (first entry) and vibrational harmonic wavenumber (ω_i, in cm^{-1}, second entry) for the van der Waals complexation modes of the Zn^{q+}Im (q = 0, 1, 2) complexes. We give their IR intensities (I, km/mol). These values were computed at the M05-2X/6-311++G(d,p) level.

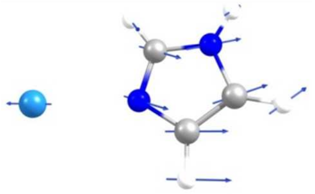
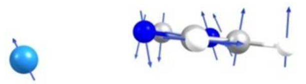
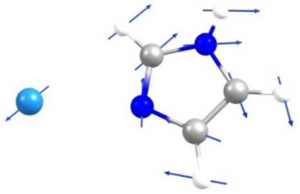
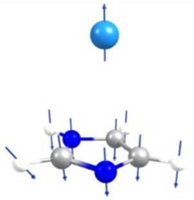
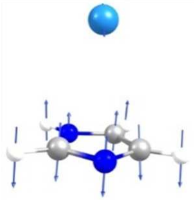
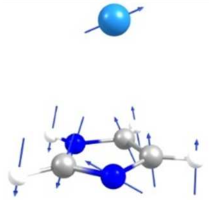
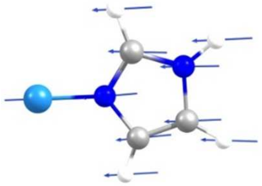
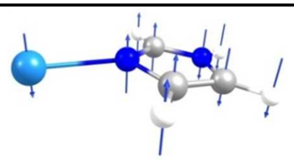
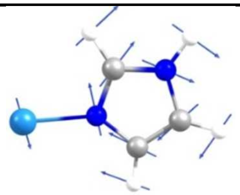
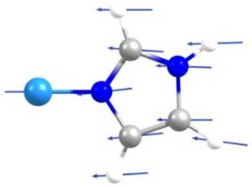
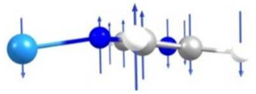
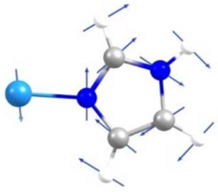
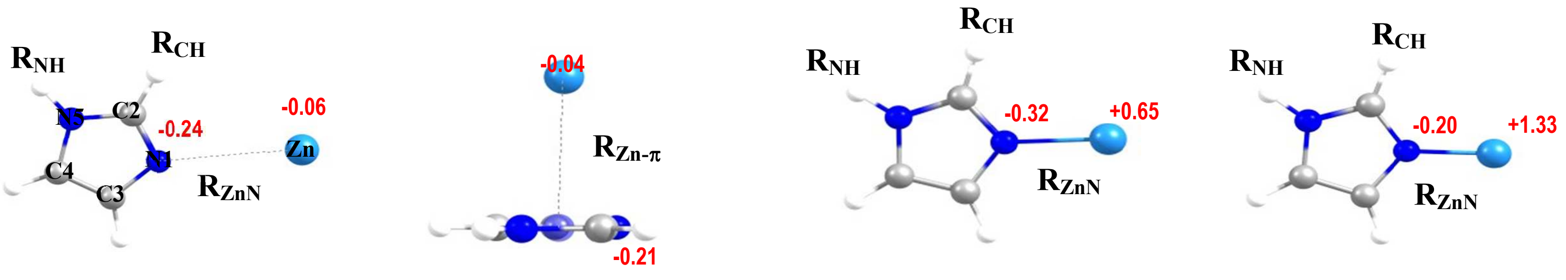
Complexes	Assignment	Stretching		Bending		Oscillating Mode	
		ν_{calc}	I	ν_{calc}	I	ν_{calc}	I
Zn^{0}Im I	$\boldsymbol{\nu_{ZnN}}$	 **41**	**5**	 **14**	**4.5**	 **47**	**5.3**
Zn^{0}Im II	$\boldsymbol{\nu_{Zn\text{-}\pi}}$	 **63**	**1**	 **73**	**11**	 **85**	**3.0**
Zn^{+1}Im	$\boldsymbol{\nu_{N\text{-}Zn^{1+}}}$	 **251**	**24**	 **120**	**3.7**	 **141**	**0.5**
Zn^{+2}Im	$\boldsymbol{\nu_{N\text{-}Zn^{2+}}}$	 **347**	**11**	 **127**	**17.6**	 **197**	**8.5**

Table 5 Calculated vibrational stretching frequencies (scaled) and complexation induced shifts for $Zn^{q+}Im$ complexes computed at the M05-2X/6-311++G(d,p) level. We give also the IR intensities of the bands (I, km/mol).

	Assignment	ν_{calc} / cm^{-1}	I	Shift / cm^{-1}		Assignment	ν_{calc} / cm^{-1}	I	Shift / cm^{-1}
Im	ν_{NH}	3518	99	3518(ν_{exp}) [a)]	**Im**	ν_{C2H}	3103	2	3110(ν_{exp})
Zn^0Im I	ν_{ZnN}	38	5		**Zn^0Im II**	ν_{ZnN}	59	1	
	ν_{NH}	3516	97	-2		ν_{NH}	3518	91	0
	ν_{C2H}	3093	0.5	-10		ν_{C2H}	3098	0.5	-5
$Zn^{+1}Im$	ν_{ZnN}	236	24		**$Zn^{+2}Im$**	ν_{ZnN}	327	10	
	ν_{NH}	3465	213	-53		ν_{NH}	3391	365	-127
	ν_{C2H}	3112	22	9		ν_{C2H}	3104	58	1

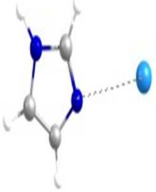
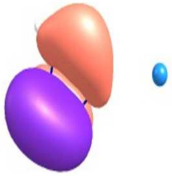
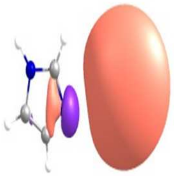
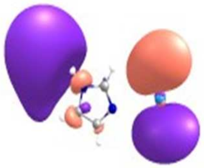
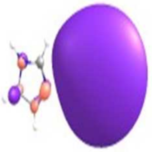
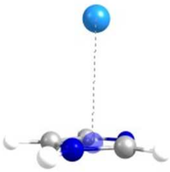
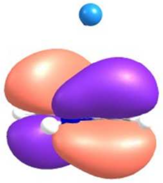
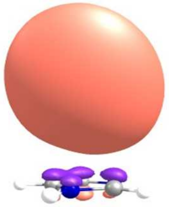
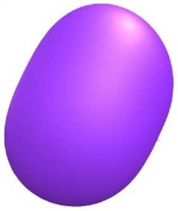
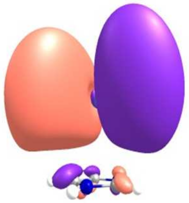
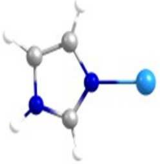
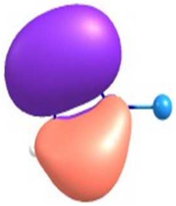
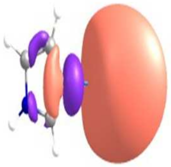
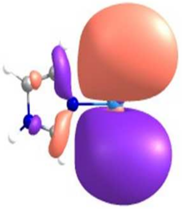
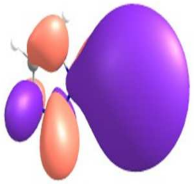
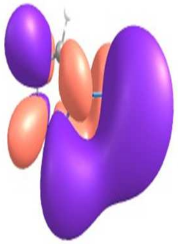
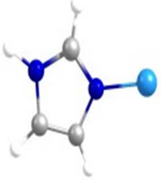
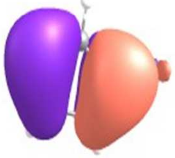
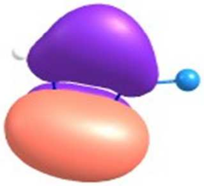
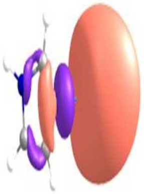
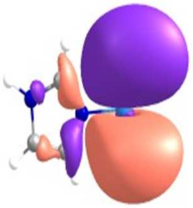
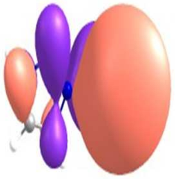
a) Ref. [62]

Figure 1 Optimized equilibrium structures of the $Zn^{q+}Im$ (q = 0, 1, 2) complexes and the definition of the parameters given in Table 1. For $Zn^{0}Im$ II, R_{CH} and R_{NH} have the same definition as in the other forms. In red, we give the charges on Zn and the unprotonated nitrogen (N1) of Im computed at MP2/6-311++G(d,p) level.



$Zn^{0}Im$ I **$Zn^{0}Im$ II** **$Zn^{+1}Im$** **$Zn^{+2}Im$**

Figure 2 Zn^{q+}Im (q=0,1,2) complexes frontier molecular orbital (isosurface density = 0.02 a.u) calculated at M05-2X/6-311++G(d,p) level.

Molecular species	Structure	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
Zn^{0}Im I						
Zn^{0}Im II						
Zn^{+1}Im						
Zn^{+2}Im						

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