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PAPER

Non-conventional hydrogen bonds: pterins-metal anions†

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In this paper, we present an analysis of the interaction of metal ions (Cu, Ag and Au) with three different pterins (pterin, isoxanthopterin and sepiapterin) to provide insights concerning the formation of conventional and non-conventional H bonds. Density functional theory calculations were performed in order to reveal the optimized structures of pterin molecules, dimers and tetramers compounds, both with and without metal anions (M). The interaction with small metal clusters (M₃) is also considered. The formation of different systems is characterized in terms of the structural parameters and hydrogen binding energies (HBE). The HBE values for pterin-M systems presented in this study lie between 22 and 60 kcal mol⁻¹ and can therefore be classified as strong conventional and strong non-conventional hydrogen bonds. The HBE with small metal clusters (pterin-M₃) are smaller than the HBE with metal atoms. Vertical electron detachment energies (VEDEs) are also reported in order to analyze the influence of the hydrogen bond on electronic properties. A direct correlation between VEDEs and HBE was found for pterin-M and pterin-M₃ complexes; *i.e.* as the VEDEs increase, the HBE also augments. The only exception is with Ag₃. The main conclusion derived from this study is that the strong non-conventional hydrogen bonds formed between pterins, dimers and tetramers do not affect the formation of conventional hydrogen bonds between pterins but they do influence the VEDEs.

Introduction

Pterins or pteridins are animal pigments that confer the yellow-red color to a number of animals.¹ They are heterocyclic compounds, analogous to guanine, which have the highest nitrogen content of any natural colorants found in the animal kingdom. Pterins are present in living systems and are essential for many biological functions in the form of antioxidants and immune cell protectors.^{2–5} It was previously reported^{6,7} that they can act as effective free radical scavengers and may also interact with metal atoms forming compounds with varying electron donor–acceptor properties. It has also been shown that pterins can self associate to form dimers, ribbons or macrocycles *via* intermolecular hydrogen bonds,^{8,9} as well as forming hydrogen bonds with the N–H groups, when ions host outside or inside macrocycles.

The interaction of metal anions and clusters with the RNA and DNA nitrogen base^{10–27} can lead to the formation of non-conventional hydrogen bonds, as first reported by Kryachko and Remacle.²⁰ These authors used small gold clusters as simple models for Au particles and concluded that “in the most stable planar base complexes, the Au–N or Au–O anchor bonds are reinforced by N–H···Au bonds”. They nominated these interactions as non-conventional H bonds. These bonds are important since they can stabilize or destabilize the nitrogen base pairs, as has been reported for gold anionic clusters interacting with the adenine–uracil base pair.^{24,26} In these systems, the extra electron is localized on the metal atom since the anionic gold atom has a stable closed-shell electronic configuration. Metal anions are the hydrogen bond acceptors and form non-conventional H bonds that modify the conventional hydrogen bonds of the nitrogen base pair. One important conclusion that has been reported previously is that metal anions, bonded to conjugated molecular systems, such as nitrogen bases of RNA and DNA, will present substantial charge-transfer effects. It has also been reported that the interactions of H bonds may modify the vertical electron detachment energy (VEDE) of the systems, *i.e.* the metal anions may function as electron donors and thereby change the properties of the compounds.

In spite of the existence of previous studies using a nitrogen DNA and RNA base, no results with pterins have been presented. Since pterins are analogous to guanine, in this work the important question refers to whether non-conventional

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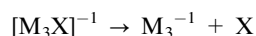
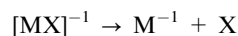
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H bonds are also present when metal anions interact with these molecules. Also, due to the similarities between pterins and guanine, these interactions may be crucial for the formation of supramolecular structures. In this paper, an analysis of the interaction of three metal anions (Cu, Ag and Au) and three different pterins (pterin (Ptr), isoxanthopterin (7-Xap) and sepiapterin (Sep)) was undertaken to provide insights on the formation of conventional and non-conventional H bonds. VEDEs are also analyzed in order to assess the influence of the hydrogen bond on electronic properties. Small anionic metal clusters (M_3) were also considered in order to see the formation of non-conventional H bonds since this type of bonds could be interesting and important from the applications perspective. We also describe the formation of different pterins, dimers and tetramers, both with and without metal anions. The main conclusion of this investigation is that the metal ion form non-conventional hydrogen bonds with pterins, dimers and tetramer, but these non-conventional hydrogen bonds do not affect the formation of conventional hydrogen bonds between pterins.

Computational details

Density functional theory as implemented in the Gaussian 03²⁸ program was used for all the calculations, using the hybrid exchange correlation functional B3LYP.^{29–31} For Ag and Au, two different pseudopotentials were used: LANL2DZ^{32–34} and Peterson-Puzzarini (PP).³⁵ For Br, Cu, C, N, O and H, two basis sets were employed: 6-311G** and 6-311++G(3df,3pd),³⁶ the Br anion was included for comparison purposes with a conventional hydrogen acceptor. The optimization of all the initial conformers was done at the B3LYP/6-311G**+LANL2DZ level. The most stable structures were re-optimized with B3LYP/6-311++G(3df,3pd)+LANL2DZ. For systems with Ag and Au, final energy was evaluated, applying a single point energy calculation at B3LYP/6-311++G(3df,3pd)+PP level. Due to the size of the systems, tetramers were calculated at the B3LYP/LANL2DZ level. All minima were characterized by frequency analysis. The applicability of the methodology was assessed, using the NH_3 and OH^- as hydrogen bond donors.

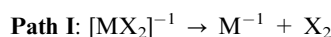
The HBE was calculated in terms of (X indicates NH_3 , OH^- or pterin molecule, M is the metal atom and M_3 is the metal clusters):



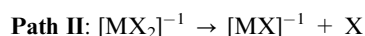
$$HBE = [E(M^{-1}) + E(X)] - (E[MX]^{-1}) \quad (1a)$$

$$HBE = [E(M_3^{-1}) + E(X)] - (E[M_3X]^{-1}) \quad (1b)$$

For dimers, the HBE was calculated by following two paths:

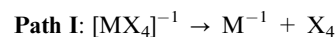


$$HBE (I) = [E(M^{-1}) + E(X_2)] - (E[MX_2]^{-1}) \quad (2)$$

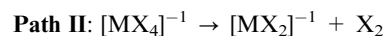


$$HBE (II) = [E([MX]^{-1}) + E(X)] - (E[MX_2]^{-1}) \quad (3)$$

For tetramers, the HBE was calculated, applying the following paths:



$$HBE (I) = [E(M^{-1}) + E(X_4)] - (E[MX_4]^{-1}) \quad (4)$$



$$HBE (II) = [E([MX_2]^{-1}) + E(X_2)] - (E[MX_4]^{-1}) \quad (5)$$

Path I evaluates the hydrogen bond between the metal anions and the dimer or tetramer. Path II provides an estimation of the strength of the hydrogen bonds between pterins or pterin dimers. It is important to note that in order to obtain HBE (II) for the tetramer (eqn (5)), $[MX_2]^{-1}$ was not optimized. We performed a single point energy evaluation of $[MX_2]^{-1}$ with the geometry that it has in the tetramer. It is not possible to use the optimized values of $[MX_2]^{-1}$ because they were calculated at a different level of theory. The optimization of $[MX_2]^{-1}$ at B3LYP/LANL2DZ generates a three dimensional structure with the metal atom lying outside the plane which is thus very different. If we employ these geometries we must also consider the deformation of the structure. We are able to accurately estimate the hydrogen bond energy, using the single point energy evaluation.

Performance of the methodology

In order to analyze the applicability of the methodology, $[AuNH_3]^{-1}$ optimized parameters calculated at the B3LYP/6-311++G(3df,3pd)+LANL2DZ level are compared with available experimental values (Supporting Information, Table 1S†). In general, experimental values are smaller than theoretical ones, but the difference is not very large and we affirm that in the case of this study, theoretical and experimental values concur. It is also important to analyze the effect of the basis set on the hydrogen bond energies (HBE). For the final energy evaluation, B3LYP/6-311++G(3df,3pd)+PP was applied. As can be seen in Table 1S,† the results concur very well with the experimental values.³⁷ We also carried out calculations on transition metal hydroxides ($CuOH$, $AgOH$ and $AuOH$), in order to compare these with experimental values and with other calculations that include both relativistic and electron correlation effects.³⁸ Our results are presented in Table 2S of the Supporting Information† and are shown to closely coincide with previous reports. Thus these comparisons indicate that our computations provide sufficiently reliable information relating to this kind of hydrogen bond.

Results and discussion

Optimized geometries

In order to search for a global minimum on the potential energy surface, we considered different positions of the metal atom. Initial conformers used for the geometry optimization are shown in Fig. 1. Fig. 2–4 illustrate the optimized structures for each system. Energy differences with respect to the most stable structure are also revealed. The most stable structures

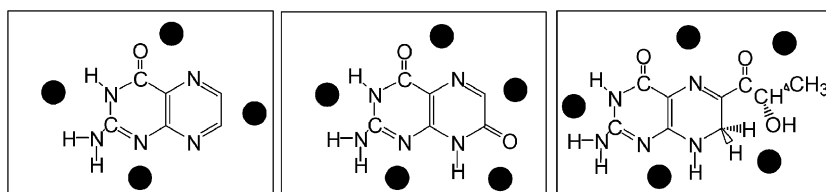


Fig. 1 Initial conformers. Black circles represent the different positions of the metal atom that were used as initial geometries.

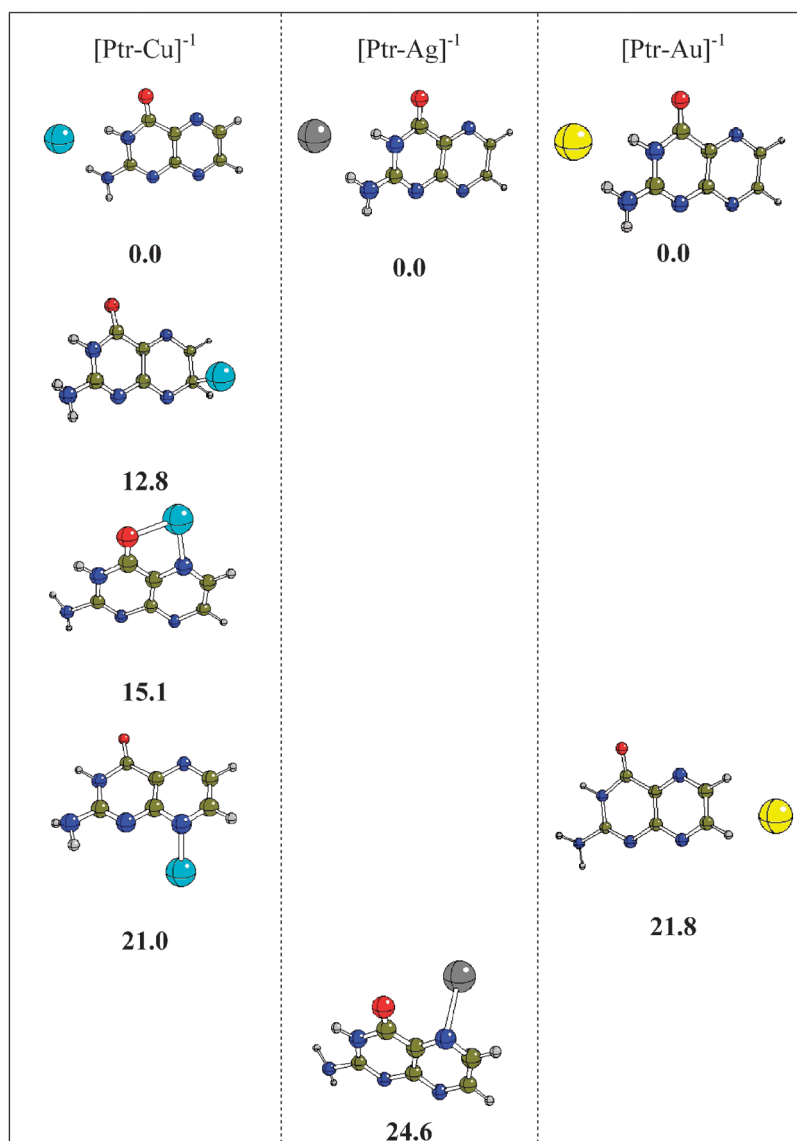


Fig. 2 Optimized structures for [Ptr-M]⁻¹. Energy differences (in kcal mol⁻¹) with respect to the most stable structure are also shown.

are all similar with only one exception: [Sep-Cu]⁻¹. The ground state of this complex has the Cu atom bonded to nitrogen and oxygen atoms of Sep. The energy difference in the case of the second stable isomer is less than 10 kcal mol⁻¹ and thus both may be present in an experiment. It is worth noting that this isomer is less stable when the metal atom is Ag. In the case of Au this isomer is not stable at all as the optimization which begins with this initial geometry ends on one of the other two structures that are shown in Fig. 4.

The atomic charges for the ground state of [Sep-Cu]⁻¹ indicate that the Cu atom is positively charged and bound to N and O which both have negative charges. For the formation of this type of compound, it is necessary to have a positive metal atom present and for this reason, its ionization energy is an important variable to be considered. The order of the metals in terms of ionization energy is Cu < Ag < Au. In fact, the ionization energy of Au is around 1.5 eV higher than the ionization energy of Cu. The energy required for the ionization

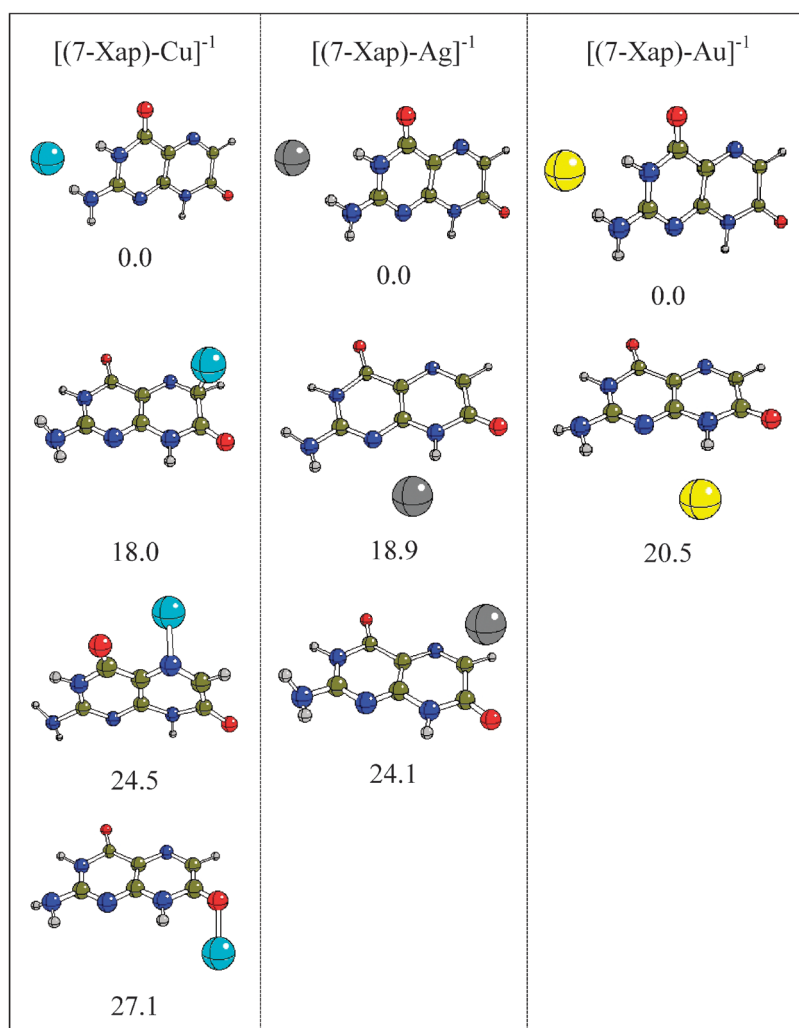


Fig. 3 Optimized structures for $[(7\text{-Xap})\text{-M}]^{-1}$. Energy differences (in kcal mol^{-1}) with respect to the most stable structure are also shown.

of Au to form Au^+ is high, and this may explain why an Au cation is not formed and consequently why it is not bonded to nitrogen and oxygen atoms of Sep. The ionization energy of Ag is 0.2 eV higher than the ionization energy of Cu. It is possible for positive Ag atoms to be formed and also to become attached to negative N and O atoms of Sep, but they are less stable than the ground state reported in Fig. 4. Therefore, the fact that the Cu ion binds to N and O of Sep is explained by taking into account that the ionization energy of the Cu is lower than the ionization energy of Ag and Au. In this paper we focus on non-conventional H bonds, hence we will proceed by discussing the second stable isomer of $[\text{Cu-Sep}]^{-1}$ and the most stable states for the other molecules. The ground states of the structures with non-conventional H bonds have the metal atom bound to two hydrogen atoms of the pterins. Therefore, two non-conventional H bonds are formed. For Ptr and 7-Xap, other conformers are less stable by a difference that exceeds 10 kcal mol^{-1} , whereas in the case of Sep with Ag and Au, we find two stable structures with similar stabilities. In the case of the second conformer of $[\text{Ag-Sep}]^{-1}$ and $[\text{Au-Sep}]^{-1}$ there are also two non-conventional H bonds. The formation of the second isomer of metal ions with

Sep, that is almost degenerate with the most stable ones, is possible due to the presence of the OH group. The two stable conformers of $[\text{Ag-Sep}]^{-1}$ and $[\text{Au-Sep}]^{-1}$ present non-conventional hydrogen bonds between the metal ions and the hydrogen atoms of the NH groups of Sep and also between the metal ions and the OH group of Sep. Similar results were found for guanine with Cu anion.¹⁰ Guanine is structurally related to Ptr. For $[\text{Cu-guanine}]^{-1}$ the most stable structure shows Cu–H non-conventional bonds and the most stable structure with copper covalently bonded to guanine is less stable by 17.5 kcal/mol .

It is evident that in the less stable structures of $[\text{Ptr-Cu}]^{-1}$, $[\text{Ptr-Ag}]^{-1}$, $[(7\text{-Xap})\text{-Cu}]^{-1}$ and $[\text{Sep-Ag}]^{-1}$, the metal atom is bonded to carbon, nitrogen or oxygen, whereas in the second and third structures of $[(7\text{-Xap})\text{-Ag}]^{-1}$ and in compounds with Au, the metal is bonded to hydrogen atoms. Stable structures of $[\text{Ptr-Au}]^{-1}$ show Au–HN (in the ground state) and Au–HC (in the second stable isomer) of non-conventional H bonds; the structure being more stable in the first case, than in the second one. The main structural difference between the two stable isomers of $[(7\text{-Xap})\text{-Ag}]^{-1}$ and $[(7\text{-Xap})\text{-Au}]^{-1}$ refers to the number of non-conventional H bonds, as the less stable

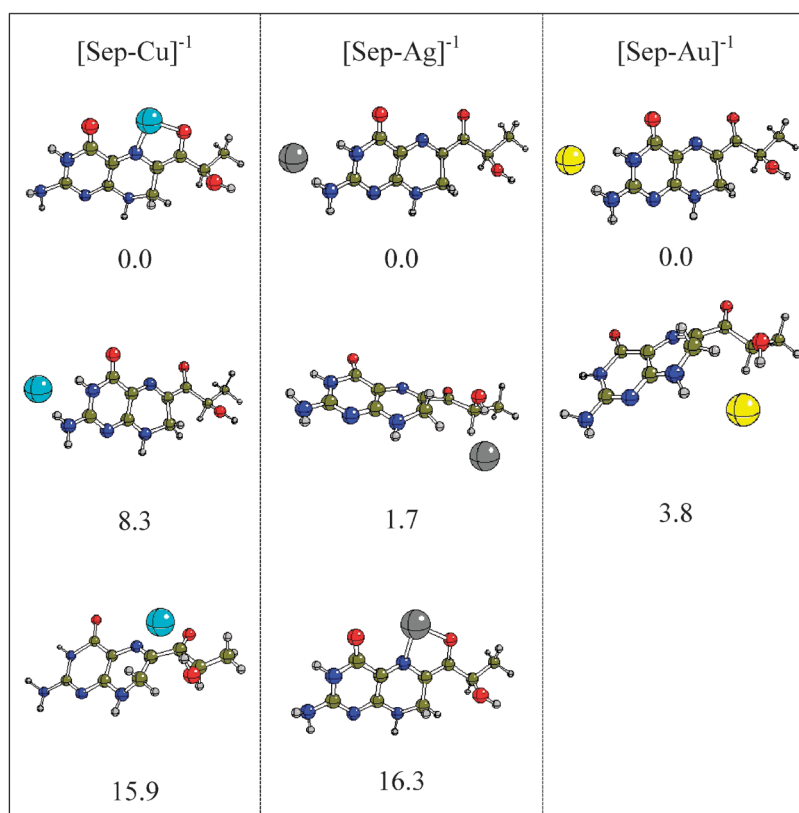


Fig. 4 Optimized structures for $[(\text{Sep})\text{-M}]^{-1}$. Energy differences (in kcal mol^{-1}) with respect to the most stable structure are also shown.

structures present only one, whereas two are present in the ground state.

In Table 1, the hydrogen bond geometrical parameters of pterins with metal anions are presented for the most stable structures. It is evident in all cases that the bond distances of M–H2 are shorter than those of M–H1, and that the M–H2–N2 bond angle is nearer the linear than M–H1–N1. Structural parameters of conventional hydrogen bonds

correlate with the strength of hydrogen bonds. It is known that strong hydrogen bonds (that may have energies between 12 and 40 kcal mol^{-1}) show linear bonds with angles measuring close to 180° and short bond distances between the hydrogen and acceptor atoms (1.2–1.5 Å). Contrarily, weak hydrogen bonds have no linear bonds (90–150°), larger hydrogen bond distances (2.2–3.2 Å) and binding energies of less than 4 kcal mol^{-1} .³⁹ Values in between indicate medium hydrogen bonds. These structural parameters are useful for classifying conventional H bonds and can also be used for non-conventional H bonds. According to the structural aspects presented in Table 1, it is possible to say that M–H1 are weak and M–H2 are medium non-conventional H bonds. In order to verify whether there is a correlation between structural parameters and the strength of the non-conventional H bond, the hydrogen bond energy (HBE) for $[\text{X-M}]^{-1}$, (X is the pterin molecule and M is the metal atom) was calculated according to eqn (1a). The results for the most stable structures are reported in Table 2. HBE values for systems with gold atoms are higher than for systems with Cu and Ag. The M–H1 and M–H2 bond distances with Au are also the shortest. This means that non-conventional H bonds with gold atoms are stronger than with the other two metals. The weakest bonds correspond to Ag, which also show the largest M–H1 and M–H2 bond distances, as presented in Table 1. Moreover, $[(7\text{-Xap})\text{-M}]^{-1}$ complexes are more stable than $[\text{Sep-M}]^{-1}$ and $[\text{Ptr-M}]^{-1}$ and likewise the non-conventional H bond lengths with 7-Xap are shorter than with the two other pterins. Even though there is an inverse correlation between the HBE and the M–H bond distance, *i.e.* as the bond length

Table 1 Hydrogen bond geometrical parameters (distances in Å and angles in degrees) for the most stable isomers

| M | Bond distances | | Bond Angles | |
|----------------------------------|----------------|------|-------------|--------|
| | M–H1 | M–H2 | N1–H–M | N2–H–M |
| $[\text{Ptr-M}]^{-1}$ | | | | |
| Cu | 2.71 | 2.33 | 148.6 | 164.5 |
| Ag | 2.77 | 2.45 | 149.3 | 163.5 |
| Au | 2.54 | 2.29 | 151.7 | 161.0 |
| $[(7\text{-Xap})\text{-M}]^{-1}$ | | | | |
| Cu | 2.76 | 2.27 | 145.5 | 165.8 |
| Ag | 2.79 | 2.41 | 147.4 | 163.7 |
| Au | 2.57 | 2.25 | 149.6 | 161.5 |
| $[\text{Sep-M}]^{-1}$ | | | | |
| Cu | 2.97 | 2.25 | 138.6 | 169.1 |
| Ag | 3.02 | 2.40 | 139.9 | 167.1 |
| Au | 2.69 | 2.24 | 146.7 | 164.3 |

Table 2 Non-conventional hydrogen bond energies (HBE, in kcal mol⁻¹) according to eqn (1a), and vertical electron detachment energies (VEDE, in eV)

| M | HBE | | | VEDE | | |
|----|-----------------------|---------------------------|-----------------------|-----------------------|---------------------------|-----------------------|
| | [Ptr-M] ⁻¹ | [(7-Xap)-M] ⁻¹ | [Sep-M] ⁻¹ | [Ptr-M] ⁻¹ | [(7-Xap)-M] ⁻¹ | [Sep-M] ⁻¹ |
| Cu | 25.0 | 29.0 | 24.3 | 2.4 | 2.6 | 2.4 |
| Ag | 23.7 | 27.4 | 22.8 | 2.5 | 2.7 | 2.5 |
| Au | 28.6 | 31.5 | 27.7 | 3.6 | 3.8 | 3.5 |

increases the HBE decreases, it is important to note that HBE differences between the systems reported in Table 2 are less than 5 kcal mol⁻¹ and therefore, it is possible to conclude that all complexes have similar stability.

The bond angles for all the systems reported in Table 2 are similar and, together with the bond lengths, indicate that M–H1 is weaker than M–H2. HBE values presented in Table 2 indicate that in the case of all systems, non-conventional H bonds are strong. Apparently, cooperative effects play an important role, as two non-conventional H bonds, one weak and one medium, form stable compounds with HBE values that are comparable to strong hydrogen bonds. Moreover, when molecules (such as [NH₃-M]⁻¹) have only one non-conventional H bond, the HBE registers half the value. These results uphold the idea of collaborative effects. In addition, the non-conventional H bonds are strong in spite of the long M–H distances, since the dominant contribution is an electrostatic attraction between the metal anion and the partially positive H atom. The metal anions in this study are closed shell atoms with sort of lone pair molecular orbitals that contribute to the stabilization of the non-conventional H bond.

The interaction of the non-conventional H bond is mainly electrostatic in nature.²⁰ For this reason it is important to analyze the atomic charge of the atoms that are involved. The analysis of the effective atomic charges was carried out using the natural bond orbital (NBO) scheme. The results are presented in Table 3, where isolated pterins are included for comparison. Evidently, the interaction with the metal anionic atom does not modify the charge distribution of pterins. The charge distribution of the molecules is practically the same, both with or without the metal ion. On the other hand, metal atoms are negatively charged. The extra electron is localized on the metal atoms, so that these metal anions present a stable closed shell electronic configuration. Previous reports^{23–26} indicated that the hydrogen bonds were able to

Table 3 NBO atomic charges for the atoms involved in the hydrogen bonds

| | QM | QH1 | QN1 | QH2 | QN2 |
|----------------------------|-------|------|-------|------|-------|
| [Ptr-Cu] ⁻¹ | -0.80 | 0.43 | -0.64 | 0.39 | -0.81 |
| [Ptr-Ag] ⁻¹ | -0.81 | 0.43 | -0.64 | 0.39 | -0.80 |
| [Ptr-Au] ⁻¹ | -0.83 | 0.43 | -0.64 | 0.40 | -0.79 |
| Ptr | — | 0.41 | -0.62 | 0.38 | -0.78 |
| [(7-Xap)-Cu] ⁻¹ | -0.78 | 0.43 | -0.64 | 0.38 | -0.81 |
| [(7-Xap)-Ag] ⁻¹ | -0.79 | 0.43 | -0.64 | 0.39 | -0.80 |
| [(7-Xap)-Au] ⁻¹ | -0.82 | 0.44 | -0.64 | 0.40 | -0.79 |
| (7-Xap) | — | 0.41 | -0.62 | 0.39 | -0.77 |
| [Sep-Cu] ⁻¹ | -0.78 | 0.43 | -0.63 | 0.37 | -0.81 |
| [Sep-Ag] ⁻¹ | -0.79 | 0.43 | -0.63 | 0.38 | -0.80 |
| [Sep-Au] ⁻¹ | -0.83 | 0.44 | -0.64 | 0.40 | -0.78 |
| Sep | — | 0.40 | -0.62 | 0.39 | -0.77 |

modify the VEDE values of the molecules. It is important to note that photoelectron detachment experiments to obtain the VEDE values are conducted by crossing a mass-selected beam of negative ions with a fixed frequency photon beam, and analyzing the resultant energy of the photo detached electrons. The anions are usually prepared in a laser vaporization source, and this produces an extra electron, that is localized on the metal atom. There is not a charge transfer process between the pterins molecules and the metal atom to create the metal anion. For the VEDEs determination, the extra electron comes from the experiment.

The VEDEs of the hydrogen-bonded anion complexes studied here were obtained by calculating the total energy of the anionic molecule, minus the total energy of the neutral molecule. We used single point energy calculations to assess the energy of the neutral molecule of the anionic optimized geometry. Results are also presented in Table 2. Evidently there is a direct correlation between the VEDEs and the HBE. For example, [Ptr-M]⁻¹ and [Sep-M]⁻¹ complexes have similar VEDE and also comparable values for HBE, whereas [(7-Xap)-M]⁻¹ has bigger VEDE, and also greater HBE. Thus, (7-Xap) forms the strongest bonds with Au⁻¹ and it also has the greatest VEDE.

In summary, metal anions such as Au, Cu and Ag form stable non-conventional H bonds with pterins, and consequently they may participate in the stabilization of macrocycle structures. The results reported in Table 2 are useful for further investigations since VEDEs can be obtained through photoelectron detachment experiments. Unfortunately, for these systems there are no experimental results reported in the literature. Nevertheless, the theoretical values reported in this paper could be helpful for future experimental characterization of these molecules.

The formation of non-conventional H bonds is interesting and important from the application perspective when anionic metal clusters are used instead of anionic metal atoms. To see the differences between the reactivity of metal atoms and clusters with pterins, small anionic metal clusters formed with three metal atoms were bonded to the Ptr molecule. We used only Ptr molecule as an example for the investigation of the electronic structure of metal clusters with pterins, since different pterins have similar bonding schemes with metal atoms, and it can be expected to show the same behavior with metal clusters. The results reported in Fig. 5 show that the optimized structures of [Ptr-M₃]⁻¹ present non-conventional H bonds, as it was found for [Ptr-M]⁻¹. The formation of two non-conventional H bonds between metal ions and H atoms stabilizes the system. HBE and the VEDE values are reported in Table 4. NBO atomic charges for the atoms involved in the hydrogen bonds are also included. It is possible to see that,

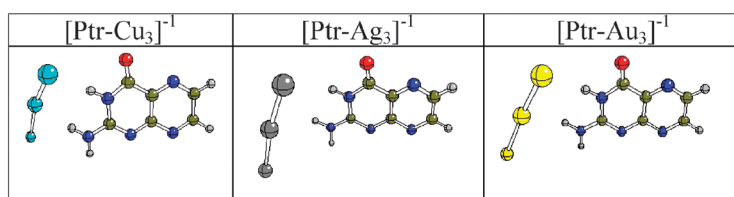


Fig. 5 Optimized structures for $[\text{Ptr-M}_3]^{-1}$.

Table 4 Non-conventional hydrogen bond energies (HBE, in kcal mol^{-1}) according to eqn (1b), and vertical electron detachment energies (VEDE, in eV). NBO atomic charges for the atoms involved in the hydrogen bonds are also reported

| M | $[\text{Ptr-M}_3]^{-1}$ | | | | |
|----|-------------------------|------|------|-----|------|
| | HBE | VEDE | QM | QH1 | QN1 |
| Cu | 12.5 | — | −0.4 | 0.5 | −1.0 |
| | — | 3.06 | −0.3 | 0.3 | −0.8 |
| Ag | 10.8 | — | −0.4 | 0.4 | −0.6 |
| | — | 4.12 | −0.2 | 0.4 | −0.7 |
| Au | 13.2 | — | −0.4 | 0.4 | −0.6 |
| | — | 4.38 | −0.2 | 0.4 | −0.7 |

with small anionic metal clusters, there is also a direct correlation between the VEDEs and the HBE, *i.e.* as the HBE increases the VEDEs also augment. The only exception is for $[\text{Ptr-Ag}_3]^{-1}$. Comparing the HBE values of $[\text{Ptr-M}_3]^{-1}$ with the correspondent results of $[\text{Ptr-M}]^{-1}$ (see Table 2) it can be seen that the bond of Ptr with metal clusters is almost half the HBE of the metal atom with Ptr. It is possible to explain these results with the comparison of the negative charge of the metals atoms that are forming the non-conventional hydrogen bonds. The atomic charge of the metal atom is twice the atomic charge of the metal atoms in the clusters because the extra electron in the cluster is distributed all over the cluster. For this reason, the HBE is smaller for anionic clusters than for metal anions. This observation confirms the idea that the main contribution on these non-conventional hydrogen bonds is electrostatic. In spite of these differences, anionic metal cluster also form non-conventional hydrogen bonds that stabilized the systems.

Conventional versus non-conventional hydrogen bonds

Pterins, as guanine, are able to form intramolecular hydrogen bonds. In order to analyze the formation of conventional H bonds and compare these with non-conventional H bonds, we optimized the dimers and tetramers of Ptr both with and without metal ions and then we calculated HBE (I) and HBE (II), by applying eqn (2)–(5). The results of the geometrical optimization are presented in Fig. (6) and (7). We also used initial geometries with the metal atom situated between the two pterins or inside the four pterins, but the optimized structures of these initial geometries are evidently 40 kcal mol^{-1} less stable, than the structures shown in Fig. (5) and (6). In Fig. 5 there are two dimers of Ptr without a metal anion, presenting two or three hydrogen bonds. Both structures have similar HBE in spite of the number of hydrogen bonds that are present in the dimer. The most stable dimers of Ptr interacting with metal anions are extremely planar.

The metal ion is in the middle of the two hydrogen atoms and forms two highly symmetric non-conventional H bonds that are of equal length. The pterins' dimer has three conventional H bonds which are almost the same length. The O–H bond is longer and the N–H bond is shorter in the case of systems with a metal ion, than for the isolated dimers. In all cases, the M–H bonds are shorter for $[\text{Ptr-Ptr-M}]^{-1}$ than for $[\text{Ptr-M}]^{-1}$ (see Table 1). The metal atomic charge is also different. It is smaller in the case of the dimer (Fig. 6) than in the case of the monomer (Table 3) when the metal atom is Cu or Ag, but remains the same in the case of Au. In Fig. 6, the HBE for non-conventional H bonds (HBE (I)) and conventional H bonds (HBE (II)) is presented. Evidently, the interaction with the metal ion (path I) is slightly stronger than the interaction between the two pterin molecules (path II). The comparison of the HBE values between the two Ptr molecules with the metal ion HBE(II) and two Ptr molecules without the metal ion (HBE) permit us to conclude that the presence of metal ions does not modify the strength of the hydrogen bonds between the two Ptr molecules, as the HBE is almost the same. It is also apparent in Fig. 6 that Au (anion) forms the strongest non-conventional hydrogen bonds, but this bond does not affect the hydrogen bonds between the two pterin molecules. The presence of the metal ion perturbs the conventional intermolecular hydrogen bonds between the pterins molecules, since the hydrogen bond distances between the two pterins are different with and without the presence of the metal ion. However, this perturbation does not affect the HBE given that one bond length increases but there is another one that decreases with the presence of the metal ion.

In Fig. 7, we report the optimized geometries for the tetramers of Ptr, both when isolated and also when interacting with metal ions. All the optimized structures are to some extent out of the plane. The hydrogen binding energy of the tetramer without metal ions (HBE) is almost twice the HBE of the isolated dimer; given that the dissociation that we are considering for the tetramer involves four hydrogen bonds, whereas there are only two in the case of the dimer. Bond distances and angles of the isolated tetramer are similar to the corresponding values for the isolated dimer. It is possible to compare the tetramers interacting with the metal ion with the corresponding M-dimers. The interaction of the metal ion with the tetramer is similar to the interaction of the metal ion with the dimer. Small differences are evident, for example the fact that M–H bond distances are shorter in the dimer than in the tetramer and that HBE (I) is greater for the tetramer than for the dimer. Comparing HBE with HBE (II), it is possible to discern that the presence of the metal ion strengthens the conventional hydrogen bonds by 3–4 kcal mol^{-1} . In the case of all these results, it is possible to conclude that metal ions form

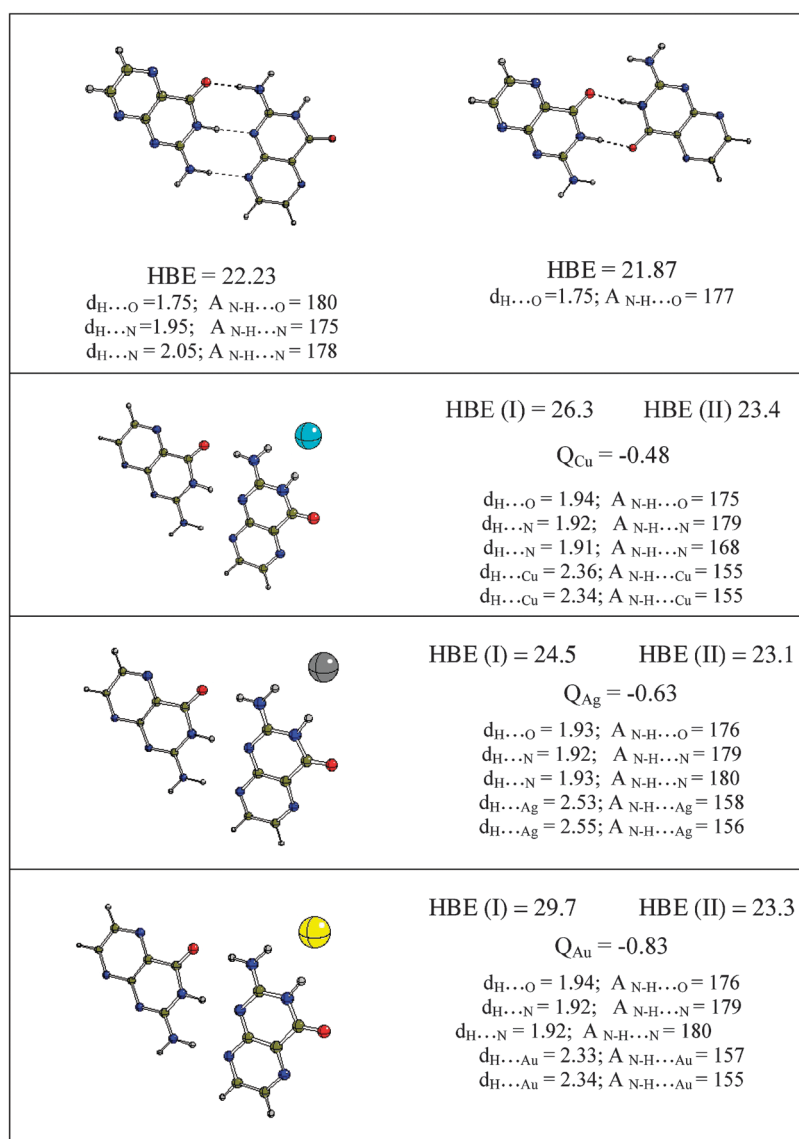


Fig. 6 Stable conformers of the dimers of Ptr and dimers of Ptr interacting with metal ions. Hydrogen binding energies (HBE, in kcal mol^{-1}) for path I (eqn (2)) and II (eqn (3)), bond distances (d , in Å), bond angles (A , in degrees) and metal atomic charges (Q_M) are reported.

non-conventional hydrogen bonds with pterins, dimers and tetramers, but these non-conventional hydrogen bonds do not affect the formation of conventional hydrogen bonds between pterins. The presence of the metal ion does not affect the stabilization of the dimers and tetramers of pterins.

Conclusions

The main interactions between the metal atom and metal clusters with the pterin molecule to form $[\text{Pterin-M}]^{-1}$ and $[\text{Pterin-M}_3]^{-1}$ compounds consist of non-conventional H bonds. In ground states of these structures, metal atoms are negatively charged and bound to two hydrogen atoms of the pterins. There are two non-conventional H bonds that can be classified from their structural parameters as weak and medium. However, the HBE values are comparable to strong hydrogen bonds. Apparently, cooperative effects take place which strengthen the non-conventional H bonds.

- The VEDEs reported in this paper are useful parameters that could be helpful for the characterization of these molecules in further experiments. There is a direct correlation between the VEDEs and the HBE for $[\text{Pterin-M}]^{-1}$ and $[\text{Pterin-M}_3]^{-1}$ systems; *i.e.* as the VEDEs increase, the HBE also augments. The only exception is with Ag_3 . (7-Xap) forms the strongest bonds with Au^{-1} and it also has the largest VEDE. This means that there is an influence of the non-conventional hydrogen bonds on the electronic properties of the molecules. This could be significant for further applications where the electron movement is an important property.

- In the case of the dimers, the interaction with the metal ion is slightly stronger than the interaction between the two pterin molecules. In the case of the tetramers, the interaction with the metal ion is not as strong as the interaction between two dimers. The presence of the metal ion does not affect the stabilization of the dimers or tetramers of pterins, but they

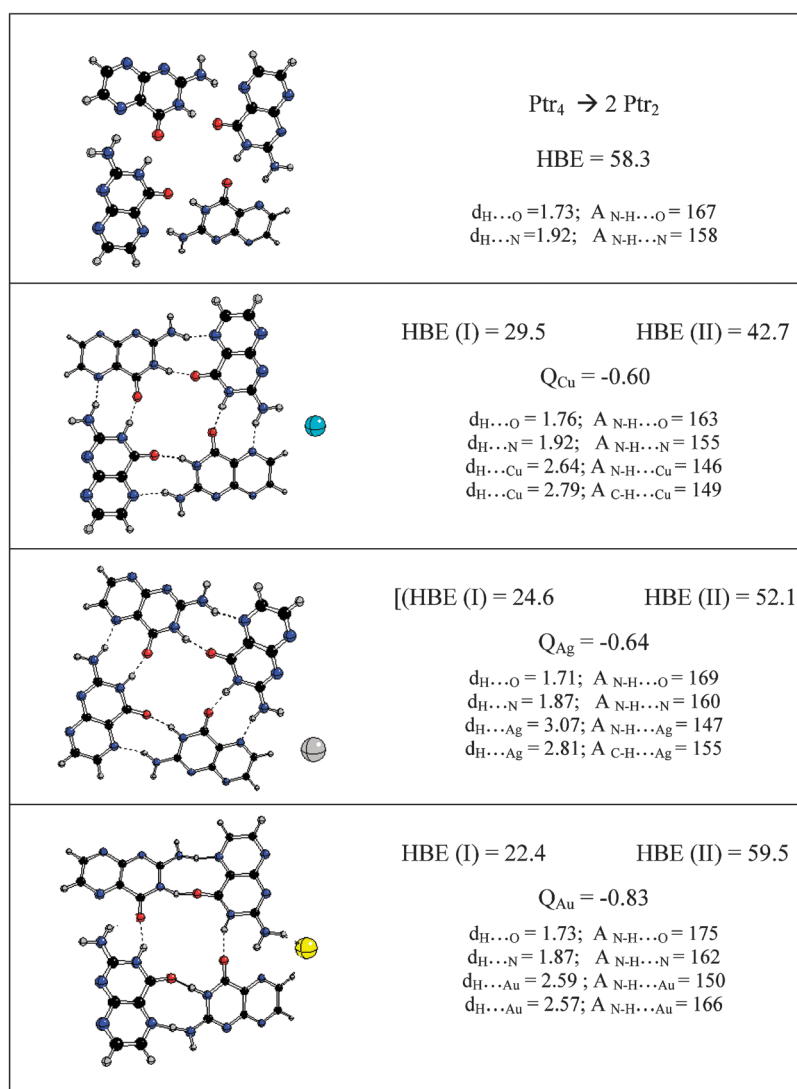


Fig. 7 Stable conformer of the tetramer of Ptr and of the tetramer of Ptr interacting with metal ions. Hydrogen binding energies (HBE, in kcal mol^{-1}) for path I (eqn (4)) and II (eqn (5)), bonds distances (d , in Å), bond angles (A , in degrees) and metal atomic charges (Q_{M}) are reported.

may play a role in the reactivity of these systems, as all metals in the compounds are negatively charged.

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References

- (a) G. E. Hill and K. J. McGraw, *Bird Coloration. Mechanisms and Measurements*, Harvard University Press, Massachusetts, 2006;
- (b) K. J. McGraw, *Anim. Behav.*, 2005, **69**, 757.
- L. W. Oliphant, *Pigm. Cell Res.*, 1987, **1**, 129.
- L. W. Oliphant and J. Hudon, *Pigm. Cell Res.*, 1993, **6**, 205.
- G. F. Grether, J. Hudon and J. A. Endler, *Proc. R. Soc. London, Ser. B*, 2001, **268**, 1245.
- K. Oettl and G. Reibnegger, *Curr. Drug Metab.*, 2002, **3**, 203.
- A. Martínez and A. Barbosa, *Theor. Chem. Acc.*, 2010, **127**, 485.
- A. Martínez and R. Vargas, *New J. Chem.*, 2010, **34**, 2988.
- J. T. Davis and G. P. Spada, *Chem. Soc. Rev.*, 2007, **36**, 296.
- L. Brunsveld, J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Supramol. Pol. Chem. Rev.*, 2001, **101**, 4071.
- A. Martínez, *J. Chem. Phys.*, 2005, **123**, 024311.
- S. V. Kornilova, P. Miskovsky, A. Tomkova, L. E. Kapinos, E. V. Hackl, V. V. Andrushchenko, D. N. Grigoriev and Y. P. Blagoi, *J. Mol. Struct.*, 1997, **408–409**, 219.
- N. Russo, M. Toscano and A. Grand, *J. Mass Spectrom.*, 2003, **38**, 265.
- W. Bal and K. S. Kasprzak, *Toxicol. Lett.*, 2002, **127**, 55.

- 14 J. V. Burda, J. Spöner and P. Hobza, *J. Phys. Chem.*, 1996, **100**, 7250.
- 15 B. A. Cerda and C. Wesdemiotis, *J. Am. Chem. Soc.*, 1996, **118**, 11884.
- 16 M. T. Rodgers and P. Armentrout, *J. Am. Chem. Soc.*, 2002, **124**, 2678.
- 17 Z. Yang and M. T. Rodgers, *J. Phys. Chem. A*, 2006, **110**, 1455.
- 18 W. Zhu, X. Luo, C. M. Pua, X. Tan, J. Shen, J. Gu, K. Chen and H. Jiang, *J. Phys. Chem. A*, 2004, **108**, 4008.
- 19 J. H. Hendricks, S. A. Lyapustina, H. L. de Clercq and K. H. Bowen Jr., *J. Chem. Phys.*, 1996, **104**, 7788.
- 20 (a) E. S. Kryachko and F. Remacle, *Nano Lett.*, 2005, **5**, 735; (b) E. S. Kryachko and F. Remacle, *J. Chem. Phys.*, 2007, **127**, 194305; (c) E. S. Kryachko and F. Remacle, *Chem. Phys. Lett.*, 2005, **404**, 142; (d) E. S. Kryachko, *J. Mol. Struct.*, 2008, **880**, 23; (e) E. S. Kryachko, A. Karpfen and F. Remacle, *J. Phys. Chem. A*, 2005, **109**, 7309; (f) E. S. Kryachko and F. Remacle, *J. Phys. Chem. B*, 2005, **109**, 22746; (g) E. S. Kryachko, *Collect. Czech. Chem. Commun.*, 2008, **73**, 1457; (h) E. S. Kryachko, *Polish J. Chem. A. Koll Festschrift*, 2009, **83**, 917; (i) E. S. Kryachko, in *Quantum Biochemistry*, ed. C. F. Matta, Wiley-VCH, Weinheim, Germany, 2009, ch 8.
- 21 P. Sharma, H. Singh, S. Sharma and H. Singh, *J. Chem. Theory Comput.*, 2007, **3**, 2301.
- 22 I. Dabkowska, J. Rak, M. Gutowski, J. M. Nilles, S. T. Stokes and K. H. Bowen Jr., *J. Chem. Phys.*, 2004, **120**, 6064.
- 23 (a) M. V. Vázquez and A. Martínez, *J. Phys. Chem. A*, 2007, **111**, 9931; (b) M. V. Vázquez and A. Martínez, *J. Phys. Chem. A*, 2008, **112**, 1033.
- 24 J. Valdespino-Saenz and A. Martínez, *J. Phys. Chem. A*, 2008, **112**, 2408.
- 25 A. Martínez, O. V. Dolgounitcheva, G. Zakrzewski and J. V. Ortiz, *J. Phys. Chem. A*, 2008, **112**, 10399.
- 26 A. Martínez, *J. Phys. Chem. A*, 2009, **113**, 1134.
- 27 A. Kumar, P. C. Mishra and S. Suhai, *J. Phys. Chem. A*, 2006, **110**, 7719.
- 28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 RE.01*, Gaussian, Inc., Wallingford, CT, 2004.
- 29 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098.
- 30 B. Mielich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
- 31 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785.
- 32 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
- 33 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
- 34 W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 284.
- 35 K. A. Peterson and C. Puzzarini, *Theor. Chem. Acc.*, 2005, **114**, 283.
- 36 (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; (b) J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss and L. Radom, *J. Chem. Phys.*, 1997, **107**, 5016.
- 37 H. Nuss and M. Jansen, *Angew. Chem., Int. Ed.*, 2006, **45**, 4369.
- 38 S. Ikeda, T. Nakajima and K. Hirao, *Mol. Phys.*, 2003, **101**, 105.
- 39 G. A. Jeffrey, *An Introduction to hydrogen bonding*, Oxford University Press, New York, 1997.