A theoretical study of intramolecular H–bonding and metal–ligand interactions in some complexes with bicyclic guanidine ligands

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ABSTRACT

The reported complexes formulated as [MnCl 2(hppH) 2](1), [FeCl 2(hppH) 2](2), and [NiCl 2(hppH) 2](3) and a new theoretically designed example, [CuCl 2(hppH) 2](4), have been used for calculations at the B3LYP/LANL2DZ/6-311G(d,p) level of density functional theory (DFT). The intramolecular hydrogen bonds (HB) N–H···Cl could followed through their physicochemical properties such as, vibrational frequency, electronic transmission in UV–Visible spectroscopy, metal–ligand donor–acceptor interactions in NBO analysis, total energy and frontier molecular orbital energy. These properties influenced by the relationship of structure and metal–ligand electron density exchange will be discussed. The computations revealed that the stronger N–H···Cl HB exists in complexes with longer M–Cl and N–iminium bonds and shorter H···Cl bond, and vice versa that confirms the shortest and longest HBs in 4 and 3, respectively. These results agree with the second–order perturbation energies obtained by NBO analysis within charge transfer from the proton–acceptor chlorine to the p orbital of the N atom. The calculated electronic absorption spectra by TD–DFT calculations show the larger Cl– to M 2+ donation in 2 and 3 in comparison with 1 and 4 that confirms the stronger HB in 1 and 4 compared to 2 and 3. In order to find the basis set effect on the structure, vibrational frequencies, and electronic transitions, we use another basis set def2-TZVP includes polarization functions for Mn element in complex 1. The obtained test results showed unremarkable differences between two basis sets LANL2DZ and def2-TZVP (cf. Figs. S2, S3 and Tables S1 and S2 in Supplementary Materials).

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1. Introduction

The hydrogen bond (HB) is a unique phenomenon in structural chemistry and biology that plays crucial roles in molecular association, function, and dynamics of the great numbers of chemical and biological compounds. The studies of systems including the H–bond have attracted growing interest during the last decades [1–5]. However, the stabilization effect of such interactions in a complex containing fragments of ligand(s) and metal has received substantially less attention. Many functional groups containing amine and imine such as oxime and guanidine ligands have the ability to form intra and intermolecular HBs playing important roles in the molecular design [6–9]. They could form N–H···X and O–H···X HBs, where X is an atom or group that contains electrons available for interaction with the acidic proton (see Fig. 1).

Guanidine derivatives are important ligands in coordination chemistry [10], especially because of their large basicity [pKa = 13.6 for HN= C(NH2)2] [11,12] and their role in biological systems [10,13,14]. Herein, we theoretically investigate structures of complexed the bicyclic guanidine (general formula: R2N(NR0)NH= C(NH2)2) 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (hppH), bearing the annular framework with the E enanti configuration of the amidine moiety which makes the NH functionality available for additional HB interaction with the X fragment to which it is coordinated. In these complexes the neutral guanidine ligand bonds through the imine nitrogen atom to a tetrahedral metal centre with additional interaction between the secondary amino NH and the metal bound halide [15]. This member of the bicyclic guanidine family is an effective enantioselective catalyst for the asymmetric synthesis of R-amino nitriles and R-amino acids [16,17]. All of the complexes described here contain an intramolecular HB involving amine functional groups (see Fig. 1). Different transition metal complexes containing guanidine ligands like hppH have been synthesized [15,18]. It has been shown that this
An extremely versatile ligand will bond to a number of main–group and transition metals and supporting a variety of geometries along with N–H−X HBs [9] i.e. from trigonal planar copper(I) [19a] and silver(I) [19b], tetrahedral iron and cobalt [9,19c] to square–planar palladium complexes [19d]. It has been proposed that the metal could reinforce the hydrogen bonds while the metal–ligand bond strength showed a reversed relation with the size of the metal ion [20]. Theoretical calculations as a good complement to experimental results have been used for better understanding of the structure and properties of synthesized complexes and for designing desired ones [21,22]. The density functional theory (DFT) method is a reliable computational approach to determine the most stable of optimized structures of the transition metal complexes, their stabilization energy, their frequencies of inter-fragment vibrations, and the potential and free energy surfaces [23]. It provides impressive results in studies of large organic and metal compounds and clusters at a relatively low computation value comparing to other post–Hartree–Fock methods.

In the present work, using DFT calculations we study geometry and electronic structure of intramolecular H–bonded complexes with the general formula Cl₂(hppH)₂ (M = Mn, Fe, Ni, and Cu). The first three are published complexes [15] ([MnCl₂(hppH)₂] (1), [FeCl₂(hppH)₂] (2), and [NiCl₂(hppH)₂] (3)) while the last is a theoretically proposed compound [CuCl₂(hppH)₂] (4) which will be compared with the others. To explore the relation between the H–bonding and donor–acceptor interactions in the complexes a quantitative analysis of the metal–ligand interactions was performed by a Natural Bond Orbital (NBO) [24] analysis. Moreover, the quantitatively and qualitatively characteristics of the metal–ligand interactions and the influenced intramolecular HBs of these complexes with metal centre size using the vibrational and TD–DFT calculations have been performed.

2. Computational details

As starting point to geometry optimization of 1–4 CIFs [15], the non–hydrogen atoms were fixed at the coordinates taken from the crystal structures and the positions of the hydrogen atoms were optimized. Full geometry optimization, vibrational frequencies, UV–Vis, and NBO calculations were performed through the DFT method at the hybrid functional B3LYP level [25–27] with the LANL2DZ (def2-TZVP for Mn in complex 1, see Supplementary Materials) basis set for the metal atoms and the 6-311G (d,p) basis set for all other atoms. Employing effective core potential (ECP) functions [28–31] such as LANL2DZ for transition metals, while using all electron basis sets for all other non–transition metal atoms has become quite popular in computations on systems containing transition metal ions because of the time saved [32]. The calculated vibrational frequencies indicated that the structures were stable (no imaginary frequencies). The computed geometrical parameters have been compared with available experimental data (see Table 1). UV–Vis spectra were calculated for the optimized geometry with a time–dependent DFT (TD–DFT) method. Singlet, doublet, and triplet excited states were considered; however as expected, all excitations to triplet states were prohibited. Net charges of all compounds are zero. The dissociation energies were corrected for BSSE using the counterpoise method [33] and for zero–point vibrational energy obtained at the B3LYP/LANL2DZ/6-311G (d, p) level. All calculations were carried out with the Gaussian 09 program package [34].
3. Results and discussion

3.1. Molecular geometries of 1–4: Theoretical point of view

The CIFs of 1, 2, and 3 with CDCDC 276690, 231326, and 276689 show that they crystallize in monoclinic and orthorhombic systems with P21/n, Fdd2, and Fdd2 space groups, respectively. Selected geometrical parameters experimentally (for 1–3) obtained from the published structures [15] and theoretically optimized (for 1–4) are collected in Table 1. The asymmetric units are the neutral monomeric complexes. The metal centre (M(II)) is four–coordinated through bonding to the imine nitrogen atoms of two monodentate hppH and two chlorides in distorted tetrahedral (for 1, 2, and 4) and square planar (for 3) geometries (see Fig. 1). It should be noted that for the optimized structures no symmetry constraints were applied. Since the structure in the solid state involves a huge network of inter–molecular interactions, the reported structural parameters for the synthesized complexes sometimes differ from the calculated ones which are based on isolated units in the gas phase. The largest differences of experimental and calculated bond lengths (Å) and angles (°) from tetrahedral to distorted square planar. It seems that hppH and chloride ligands move far away thereby changing the Cl–Ni–Cl and N–Ni–N bond angles from 116.08 and 103.81° (Exp.) to 175.25 and 175.71° (Calc.) and reinforcing a double HB (see Table 1). The lesser distortion of this torsion angle (1, 26.13 to 121.42; 2, 146.64 to 143.59) could be followed in the isostructural complexes 1 and 2. However, the largest difference of Exp. and Calc. N–H–Cl in 1 and 2 are 0.28 and 0.35 Å, respectively (see Table 1). Based on geometrical parameters (H–A and D–A bond lengths and the <DHA angle) and the electron density concept on the D and A groups, HBs can be classified into three categories, namely strong, moderate, and weak [1] and on this basis the HBs in complexes 1–4 belong to the moderate class (Table 1). The optimized structures of MCl2(hppH) show strong metal–ligand bonds as indicated by very short M–N(Namine) distances (1, 2.08; 2, 1.98; 3, 1.93; and 4, 2.00 Å, respectively), being below the sum of covalent radii of the bonded atoms (1, 2.20; 2, 2.03; 3, 1.95; and 4, 2.03 Å, respectively). The covalent radii of these metals show the trend of Ni < Cu < Fe < Mn. The above mentioned moderate HBs could be confirmed by significantly elongation of N–H bond lengths in the optimized structures (in parenthesis) as compared to the experimental ones [1, 0.823 (1.201); 2, 0.786 (1.017); 3, 0.803 (1.021); 4 (1.021)]. According to the crystal field stabilization energy (CFSE) and Jahn-Teller effect, the M–X bond length (X = Cl, N) in experimental and calculated distorted tetrahedral complexes 1–4 could be ordered as Cu–X > Mn–X > Fe–X > Ni–X. The optimized structures confirm this trend (see Fig. 1). Regarding the crystallographic and optimized structures of these complexes, elongation of M–Cl correlates with a shortening of H–Cl and the longer M–N(Namine) bond is accompanied by a shorter HB, and vice versa that confirms the shortest and longest HBs in 4 and 3, respectively (see Table 1 and Fig. 1).

The vibrational spectra show different frequencies assigned to the important functional groups of 1–4. The important features of their IR spectra (omitted) are the symmetric stretching of ν(C=N(Namine)) (Exp. 1602–1626, Calc. 1629–1637 cm–1) and ν(N(Namine)=H) (Exp. 3351–3366, Calc. 3356–3457 cm–1) [35–37]. Other essential characteristic frequencies of 1–4 are compared in Table 2 from which it can be concluded that the experimentally recorded vibrational frequencies are in good agreement with calculated ones at B3LYP/LANL2DZ/6-311G (d, p) method. The test calculations about complex 1 showed this consistency with the optimized structure at B3LYP/def2-TZVP/6-311G (d, p) experimental one (see Supplementary Materials). The low energy shift of the ν(C=N(Namine)) stretching frequency (corresponding shift in free

<table>
<thead>
<tr>
<th>Table 1</th>
<th>selected experimental and calculated bond lengths (Å) and angles (°) for B3LYP/LANL2DZ/6-311G (d, p) optimized structure of 1–4.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>M–N</td>
<td>2.107</td>
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<tr>
<td>M–X</td>
<td>2.368</td>
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<tr>
<td>C=N(Name)</td>
<td>1.354</td>
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<tr>
<td>C–NHC</td>
<td>1.348</td>
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<tr>
<td>C–NR2</td>
<td>1.351</td>
</tr>
<tr>
<td>H–Cl</td>
<td>2.458</td>
</tr>
<tr>
<td>Cl–Cl</td>
<td>2.458</td>
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<tr>
<td>N(Namine)=H–Cl</td>
<td>172.67</td>
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<tr>
<td>N–M–N</td>
<td>108.69</td>
</tr>
<tr>
<td>Cl–M–Cl</td>
<td>110.67</td>
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<tr>
<td>N–M–Cl</td>
<td>107.97</td>
</tr>
<tr>
<td>N–N–Cl</td>
<td>110.77</td>
</tr>
<tr>
<td>N–N–Cl</td>
<td>110.77</td>
</tr>
<tr>
<td>N–M–Cl</td>
<td>107.97</td>
</tr>
</tbody>
</table>

The abbreviations are, vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Calculated vibrational frequencies with B3LYP/LANL2DZ/6-311G (d, p) for optimized structures of 1–4 and free guanidine ligand.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assignments</td>
<td>1</td>
</tr>
<tr>
<td>M–Cl sym-str.</td>
<td>256.7 vw</td>
</tr>
<tr>
<td>M–N(Namine) sym-str.</td>
<td>245.9 vw</td>
</tr>
<tr>
<td>CH2 bend.</td>
<td>1476.7 m</td>
</tr>
<tr>
<td>C=NR2 str.</td>
<td>1562.4 vs</td>
</tr>
<tr>
<td>N–H str. (from N–H Cl HB)</td>
<td>3370.6–3371.2 vs</td>
</tr>
</tbody>
</table>
hhpH = 1641(Exp), 1694.6 (Calc cm\(^{-1}\)) is consistent with bonding to a metal centre via the imine rather than the amine nitrogen [35]. Moreover, the strong shift of v(Nimine–H) signal in synthesized [35–37] and optimized structures of 1–4 comparison with free hhpH (Exp. 3419 [38], Calc. 3610 cm\(^{-1}\)) is indicative of N–H···Cl HB formation. Based on the computed IR spectra the weakest and strongest N–H bond result in shortest and longest H···Cl for 4 and 3, respectively which confirms the above mentioned subject (cf. Tables 1 and 2). Generally, HBs can be estimated by the bond lengths e.g. N–H···Cl and respective angle (<NHCl), however because of complexity of the issue, just according to the structural parameters, its strength could not truly be compared.

3.2. Metal-ligand and HBs interactions

3.2.1. NBO analysis

A scientific method such as NBO analysis [24] could be performed for understanding the covalent and non-covalent interactions such as HBs [20,39–42]. During H-bonding, based on its definition, electrons may transfer between the donor (D) and acceptor (A) groups (D–H···A). This charge transfer (CT) and generally the attractive metal–ligand and HBs interactions can be characterized by the second–order perturbation energies, E(2), on the basis of the natural atomic charges and the donor–acceptor interactions [24].

\[
E(2) = -n_{\sigma} \left[ \sigma F_{\sigma} \right] = -n_{\sigma} \frac{F_{\sigma}^2}{\Delta \epsilon}
\]

where \(F_{\sigma}\) is the Fock matrix element between the NBO i(\(\sigma\)) and j (\(\sigma'\)), \(\epsilon_{\sigma}\) and \(\epsilon_{\sigma'}\) are the energies of \(\sigma\) and \(\sigma'\) NBOs, and \(n_{\sigma}\) is the population (a lone pair in the bond). On the other hand, a delocalization energy gap between donor \(\sigma \) to acceptor \(\sigma'\) orbitals enhances the CT from \(\sigma\) to \(\sigma'\) increasing E(2) and making the interaction stronger. However, the summation of all influencing parameters should be considered.

As mentioned before, although the strength of N–H···Cl could be followed through geometrical parameters of itself and its surroundings (Table 1), HB formation energy should be estimated from the metal–ligand donor–acceptor interactions in NBO analysis given in Table 3: these are the longer N–H bond, the shorter Nimine···Cl and H···Cl, and longer M···Cl and M–Nimine bonds in the stronger H–bonded [CuCl(hppH)]\(_2\) [4] especially with respect to the Ni complex (3). The considerable lengthening of the N–H bonds is caused by CT from the proton–acceptor chlorine to the \(\pi^*\) orbital of the N–H bond. This charge transfer can be characterized by the second–order perturbation energies obtained from NBO [24], giving values of 113.39, 90.96, 89.58, and 51.30 kJ/mol for HBs formation in 4, 2, 1, and 3 complexes, respectively. The calculated formation energies, E(2), and geometrical parameters of HB of the crystallographic and optimized structures have a good consistency (see Fig. 1 and Tables 1 and 3). The very stable title complexes show large dissociation energies (around 81,000 kJ/mol, see Table 3) of [MCl(hppH)]\(_2\) → \(M^{2+} + 2(Cl^{-} + hhpH)\). These rather high values can be attributed to the very low stability of the resulting ions in vacuum. The dissociation energies increase from M = Mn to Cu due to increasing the strength of Nimine, M = Cl, and respective HB bonds (cf. Tables 1 and 3).

The formally M\(^{2+}\) metal ions, Cl\(^{-}\), and Nimine in these complexes have natural charges of around +0.8 to 0.45, −0.53 to −0.61, and −0.58 to −0.69 e, respectively. The smaller positive charge of Ni and Fe and smaller negative charge of Cl\(^{-}\), and Nimine in 2 and 3 complexes indicate stronger donation from the chloride and hhpH ligands in these two complexes as compared with the others under study. These results confirm the shorter bond lengths within Fe and Ni in 2 and 3 and vice versa in 1 and 4. E(2) calculated energies (cf. Table 3) point to the significant CT from the ligand to the metal indicating also that the opposite process, the metal–to–ligand back–donation, must be much less. Comparison to the free hhpH, this ligand in complexes 1 and 4 coordinates by a more negatively charged Nimine (around −0.7 e) while in complexes 2 and 3 by a less negatively charged Nimine (around −0.6 e). Obviously, in the latter two complexes the coordination of L must be facilitated by stronger Nimine–M donor–acceptor interactions which are reflected by the total ligand charges (qL) in Table 3 where the hppH ligands have larger positive charges (around +0.3 e) in 2 and 3 compared with the ligands in 1 and 4 (around +0.2 e). However, the electrostatic attraction between the M\(^{2+}\), Nimine, and Cl\(^{-}\) playing probably a secondary role beside the D–A interaction.

The following D–A interactions of a Lewis model framework can operate between M\(^{2+}\) and the hhpH and chloride ligands in the title complexes:

- σ–donation from the lone pairs (LP) of Nimine and Cl\(^{-}\) to unfilled p and or d orbitals of M\(^{2+}\).
- π–donation from the π orbitals of C–Nimine double and single bonds to unfilled p orbitals of M\(^{2+}\).
- π–back–donation from occupied d orbitals of M\(^{2+}\) to anti–bonding π* orbitals of C–Nimine bonds and unfilled p* of Nimine–M.

Regarding the second–order perturbation energies obtained from NBO in Table 3 the ligand–to–metal σ–donation was found to be the major component accompanied by minor π contributions. The quantitative data of the CT interactions given in Table 3 justify

| Table 3 | Dissociation energy, computed natural charges, and charge transfer interactions in the studies complexes 1–4 |
|------------------|----------------------------------|-----------------|---------------|---------------|-------------------|
|                  | 1                               | 2               | 3             | 4             | 0.597 0.560 0.530 0.612 – |
|                  | D\(_{\text{N}}\)                | 81115.1         | 81267.9       | 81534.1       | 81649.3          |
|                  | q\(_{\text{M}}\)               | 0.793           | 0.560         | 0.454         | 0.771            |
|                  | q\(_{\text{Cl}}\)              | −0.597          | −0.578        | −0.530        | −0.612           |
|                  | q\(_{\text{Nimine}}\)          | −0.678, −0.688  | −0.588        | −0.584        | −0.612, −0.621   |
|                  | q\(_{\text{Cl}}\)              | −0.634          | −0.641        | −0.640        | −0.631, −0.651   |
|                  | q\(_{\text{H}}\)               | 0.434           | 0.434         | 0.432         | 0.437, 0.391    |
|                  | q\(_{\text{Nimine}}\)          | 0.434           | 0.434         | 0.432         | 0.437, 0.391    |
|                  | q\(_{\text{H}}\)               | 0.205           | 0.289         | 0.305         | 0.228, 0.00     |
|                  | E(2) \(\text{LP Cl(p)}\ → \sigma(N–H)\) | 89.58           | 90.96         | 51.30         | 113.39           |
|                  | E(2) \(\pi(\text{C=\text{Nimine}})\ → \text{LP M(p)}\) | 27.61           | 51.80         | N.F.          | 68.03            |
|                  | E(2) \(\pi(\text{CH}_{2}–\text{Nimine})\ → \text{LP M(p)}\) | 32.22           | 49.79         | N.F.          | 41.67            |
|                  | E(2) \(\text{LP Nimine} (s)\ → \text{LP M(p)}\) | 28.76           | 46.80         | 55.62         | 17.35            |
|                  | E(2) \(\text{LP Cl(s)p)}\ → \text{LP M(p,d)}\) | 270.75          | 301.84        | 720.40        | 134.39           |
|                  | E(2) \(\text{LP M(d)}\ → \pi(\text{C=\text{Nimine}})\) | 14.10           | 27.87         | 24.69         | 23.10            |
|                  | E(2) \(\text{LP M(d)}\ → \pi(\text{CH}_{2}–\text{Nimine})\) | 30.42           | 17.15         | 12.26         | 37.74            |
|                  | E(2) \(\text{LP M(d)}\ → \pi(\text{CH}_{2}–\text{Nimine})\) | N.F.            | 10.54         | 10.04         | 8.37             |

\(^4\) From NBO analysis. Second order perturbation energies (E(2)) donor → acceptor in kJ/mol. N.F.: Not Found.
that the main donor–acceptor interaction is the donation from the LP of the Cl⁻. The donation is somewhat larger in complexes 2 and 3 and results in the somewhat smaller negative charge of chloride ligands in these complexes in comparison with complexes 1 and 4. Obviously, in the latter two complexes the larger donation from the LPs of chlorine to the π⁺ orbital of the N–H bond form stronger HBs. The other charge transfer interactions are weaker by an order of magnitude. The data prove the minor importance of the metal–to–ligand back–donation in the title [MCl₂(hppH)₂] complexes. However, the π⁺→back–donation from metal to unfilled p⁺ of N imine is larger for 4 and 1 than those ones in 2 and 3 that increases positive charge of the metal centre, weaken the respective M–N₃imine bond length, and in conclusion it could reinforce the related H⋯Cl hydrogen bonds in 1 and 4 complexes. The other metal–ligand donor–acceptor interactions are not very different for 1–4 complexes.

3.2.2. Electronic spectrum

To investigate the electronic properties of 1–4, molecular orbital calculations with natural population analyses (NPA) based on the optimized ground state geometry have been performed. The optimized structures of them have 101, 101, 102, and 103 occupied molecular orbitals (MOs) within doublet, singlet, singlet, and doublet electron multiplicity, respectively. The complementary information could be found in Supplementary material. The frontier molecular orbitals (FMOs) can be useful for attributing the calculated UV–Vis bands to the respective electronic transitions and in conclusion comparing the involved metal–ligand interactions. The

![Table 4](image)

Calculated electronic data for 1–4.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Wave length (nm)</th>
<th>ΔEₓ (eV)</th>
<th>Oscillator strength</th>
<th>Electronic transition</th>
</tr>
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<tr>
<td>1</td>
<td>211.87</td>
<td>5.84</td>
<td>0.034</td>
<td>99a → 107a</td>
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<td></td>
<td>252.56</td>
<td>4.90</td>
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<tr>
<td></td>
<td>254.18</td>
<td>4.87</td>
<td>0.047</td>
<td>101a → 106a</td>
</tr>
<tr>
<td></td>
<td>272.31</td>
<td>4.55</td>
<td>0.024</td>
<td>98a → 109a</td>
</tr>
<tr>
<td>2</td>
<td>223.77</td>
<td>5.53</td>
<td>0.130</td>
<td>101a → 109a</td>
</tr>
<tr>
<td></td>
<td>226.62</td>
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<td></td>
<td>246.80</td>
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<td>0.045</td>
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<td>3</td>
<td>200.10</td>
<td>6.19</td>
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<tr>
<td></td>
<td>222.60</td>
<td>5.56</td>
<td>0.403</td>
<td>92a → 103a</td>
</tr>
<tr>
<td></td>
<td>239.76</td>
<td>5.16</td>
<td>0.263</td>
<td>102a (b) → 104a (b)</td>
</tr>
<tr>
<td>4</td>
<td>206.16</td>
<td>6.00</td>
<td>0.183</td>
<td>93a → 103a</td>
</tr>
<tr>
<td></td>
<td>311.80</td>
<td>3.97</td>
<td>0.014</td>
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</tr>
<tr>
<td></td>
<td>372.51</td>
<td>3.32</td>
<td>0.073</td>
<td>99b → 103b</td>
</tr>
</tbody>
</table>
main calculated wavelengths of 1–4 have been collected in Table 4 (see Tables S1 and S2 in Supplementary materials for complex 1 calculated at B3LYP/def2-TZVP/6-311G (d, p)). The experimental UV–Vis spectra for 1–4 complexes are not found in the literature. As mentioned, *vide supra*, one of the main donor–acceptor interaction is the donation from the LP of the Cl/C0 to M2+. Therefore, the main electronic band in the pertinent spectrum; comparable between complexes 1–4; related to Cl− → M ligand–to–metal charge transfer (LMCT) appears at 211.9, 223.8, 239.8, and 206.2 nm for 1–4, respectively (cf. Fig. 2). These bands can be described as n → n from LP of Cl− (s, p) to unfilled p and or d orbitals of M2+ (see Fig. 3). This trend confirms the larger donation in complexes 2 and 3 resulting in smaller negative charge on the chloride ligands in these complexes as compared

![Frontier molecular diagrams for 1 to 4 involving in CT obtained according to the B3LYP/6-311G (d, p)/LANL2DZ.](image-url)
4. Conclusion

The formation of intramolecular HBs has very pronounced effects on the molecular structure and properties. We have presented here the first systematic DFT theoretical study of bis(bicyclic guanidine) complexes of Mn, Fe, Ni, and Cu, [MCl2(hpH2)], focusing on the hydrogen bonding and metal–ligand interactions. The optimized structures have good agreement with the experimental ones. However, the largest differences of experimental and calculated symmetry geometry occurred in 3 due to changing of geometry from tetrahedral to distorted square planar.

According to the crystal field stabilization energy (CFSE), Jahn-Teller effect, and covalent radii of the metal centres, the resulting bond length of M–X (X = Cl, N) in 1–4 could be ordered as Cu–X > Mn–X > Fe–X > Ni–X. Therefore, elongation of M–Cl coupled with shortness of H–Cl and related HBs and vice versa confirms that the shortest and longest HBs are in 4 and 3, respectively. Consequently, the differences in the radii of the metals determine the differences in the lengths of the HBs. The nature of the metal-ligand and N–H–Cl HB interactions were evaluated by NBO analysis. HB could be characterized by the second–order perturbation energies because of charge transfer from the proton–acceptor chloride to the π’ orbital of the N–H bond resulting in the considerable lengthening of the N–H bonds. HB formation energy, E(2), shows the strength order of formed HB as 4 > 2 > 1 > 3. The calculated formation energies and geometrical parameters of HB of the crystallographic and optimized structures have a good consistency. However, the computed E(2) revealed the predominance of the Cl–M σ–donation and the secondary importance of the π–donation from C=Cl to M, π–back donation from M to the anti–bonding π’ orbitals of the C=Cl and N=Cl CT interactions. Based on calculated UV–Vis spectra of 1–4 complexes the main donor–acceptor interaction as the donation from the LPS of the Cl– to M2+ indicates the larger donation in complexes 2 and 3 bearing Fe and Ni metal centres in comparison with complexes 1 and 4. Because of more electronegativity and effective nuclear charge of Ni than Fe and Mn, its complex (3) should have intensity and lower energy of ligand to metal charge transfers (LMCTs) with higher wave lengths. However, the opposite trend in π–back–donation from M2+ to ligand (MLCT) should be concluded which the larger donation in complexes 1 and 4 in comparison with complexes 2 and 3 found. It should be noted that the calculations of optimization, vibrational frequencies, and charge transfers in UV–Vis spectrum of complex 1 at B3LYP/def2–TZVP/6–311G (d, p) method did not shown permanent differences with the same calculations at B3LYP/LANL2DZ/6–311G (d, p) (see Supplementary materials).

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