1. Introduction

Weak interactions, different from traditional chemical bonds, are much weaker and have lower interaction distance than corresponding covalent bonds. Nevertheless, they are no less important and play crucial roles in chemical and biochemical research, including molecular recognition, molecular medicine, functional materials design, catalysis, etc. Besides, weak interactions such as van der Waals forces, hydrogen bonding, π–π stacking effect, etc., are of great significance in the formation of supramolecular systems. In recent work, halogen bonding has been used as an efficient tool to control the emission color of bimetallic silver-gold structures. Liefgrig and co-workers reported the supramolecular self-assembled isostructural crystalline salts PT(1)X (X = Cl, Br) which are formed through halogen bonding interactions. Weak interactions were also proved to play a part in transporting K⁺ cations across lipid bilayer membranes. In addition, it has been found that the cooperative effects of multiple weak interactions help to reinforce each other. The extensive applications of weak interactions have been invoking a growing number of related research studies, which not only put forward various new forms of intermolecular or intramolecular interactions, but aid in understanding their origins.

Hydrogen bonding is one of the most common weak interactions and was first proposed in early 20th century, and is still an active topic of scientific research due to its importance in many chemical and biological processes. In general, a hydrogen bond has the form of X–H···Y, where the Y moiety interacts with the proton donor through its lone pair(s). Hydrogen bond interaction has an intrinsic directionality, and is characterized by saturaibility. In recent years, many different types of untraditional hydrogen bonds have been developed by involving diverse electron donors including conjugated molecules, radicals, metal hydrides, and even a localized electron. Correspondingly, the concepts of π-hydrogen bond, single-electron hydrogen bond, dihydrogen bond, and electron hydrogen bond have been raised successively.

Owing to the electronic similarity among lithium, sodium, and hydrogen elements, efforts have also been devoted to exploring the possibility that lithium or sodium salt molecules serve as Lewis acids to interact with electron donors. Consequently, the existence of lithium bonding and sodium bonding interactions has been put forward. In 2009, Yáñez and co-workers further enriched the study of non-covalent interactions with a series of beryllium bonding systems in which the BeX₂ (X = H, F, Cl, OH) molecules take the role of electron acceptor. As an analog of beryllium bonds, magnesium bond was theoretically predicted shortly afterwards. Different from beryllium and its compounds, the magnesium-containing complexes are non-toxic, which renders their experimental identification much more practicable. Besides, magnesium is an indispensable element in all the organisms and takes part in many important biochemical processes. Thus, the in-depth study of all sorts of magnesium bonding systems may provide meaningful references for biological and environmental chemistry studies.

In the present work, we aim to gain a fundamental understanding of the interaction between magnesium salt molecules.

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The complexes formed between MgX₂ (X = F, H) molecules and alkyl radicals Y (Y = CH₃, CH₂CH₃, CH(CH₃)₂, and C(CH₃)₃) have been characterized by using quantum chemical methods. The binding distance in all cases is less than the sum of vdW radii of Mg and C, indicating the formation of a non-covalent interaction, namely single-electron magnesium bond. Energy decomposition analysis reveals that electrostatic and polarization contributions are the major components responsible for the stability of the studied complexes. According to interaction energy, atoms in molecules, and independent gradient model analyses, methyl substitution on electron donor Y imposes a positive effect on its complexation with MgX₂. When compared with other nonbonded interactions, the single-electron magnesium bond is found to have strength comparable to those of the single-electron beryllium bond and π-magnesium bond.
and free radicals since the latter are known to play a crucial role in chemistry, especially organic chemistry, atmosphere chemistry, and biochemistry. By using quantum chemical calculations, the formation of single-electron magnesium bond between MgX₂ (X = F, H) and a series of alkyl radicals (methyl, ethyl, isopropyl, and tertiary butyl) was characterized in detail and compared with other noncovalent interactions. Besides, methyl substitution effect on structure and bonding of the resulting complexes was analyzed as well.

2. Computational details

The geometries of the X₂Mg···Y [X = F, H; Y = CH₃, CH₂CH₃, CH(CH₃)₂, and C(CH₃)₃] complexes and involved monomers were optimized at the MP2/aug-cc-pVTZ level with using the counterpoise procedure. Harmonic vibrational frequency analysis was performed at the same level to confirm that these structures are local minima on their respective potential energy surfaces. Natural bond orbital (NBO) analysis was performed at the MP2 level to examine the charge transfer between MgX₂ (X = F, H) and the alkyl radicals. In this work, the (∆S²) values are 0.7501 for all the open-shell calculations, indicating negligible spin contamination. The above calculations were carried out by using the GAUSSIAN 09 program.

The Bader’s quantum theory of atoms-in-molecules (QTAIM) was carried out to characterize the chemical bonding of the studied complexes. By the aid of Multiwfn program, the bond critical points (BCPs) were found through the analysis of wave function. Meanwhile, the electron density ρ(r) and its corresponding Laplacian (∇²ρ) at the BCPs were obtained. To intuitively show the studied single-electron magnesium bond in real space, we applied the independent gradient model (IGM) method (embedded in the Multiwfn program) in combination with the visual molecular dynamics (VMD) program. With basis set superposition error (BSSE) correction, intermolecular interaction energies of the X₂Mg···Y complexes were obtained at the CCSD(T)/MP2/aug-cc-pVTZ level. To provide more insight into the nature of interaction between MgX₂ and radical molecules, the localized molecular orbital energy decomposition analysis (LMOEDA) were performed by using the GAMESS program package. According to LMOEDA, the total interaction energy of a complex is composed of electrostatic (∆Eₑlstat), exchange-repulsion (∆Eₑx+rep), polarization (∆Eₑpol), and correlation (∆Eₑdisp) contributions, as shown in eqn (1)

\[ ∆E_{int} = ∆E_{elstat} + ∆E_{ex+rep} + ∆E_{pol} + ∆E_{disp} \] (1)

In this work, the first three components were computed at the SCF level while the ∆Eₑdisp term was obtained at the MP2 level.

3. Results and discussion

3.1 Geometric structures and single-electron magnesium bonds

The optimized structures of the X₂Mg···Y [X = F, H; Y = CH₃, CH₂CH₃, CH(CH₃)₂, and C(CH₃)₃] complexes are shown in Fig. 1, and the important geometrical parameters are presented in Table 1. For comparison, the geometrical structures of corresponding monomers are presented in ESI (Fig. S1†). The NPA

| Complex | Symmetry | L (Å) | α (°) | ∆Eₑlstat (kcal mol⁻¹) | ∆Eₑx+rep (kcal mol⁻¹) | ∆Eₑpol (kcal mol⁻¹) | ∆Eₑdisp (kcal mol⁻¹) |
|---------|----------|-------|-------|-----------------------|------------------------|---------------------|----------------------|
| I       | C₄       | 2.573 | 163.0 | 1.778                 | 1.779                  | 0.0                 |
| II-1    | C₄       | 2.509 | 160.1 | 1.781                 | 1.781                  | 32.2                |
| II-2    | C₄       | 2.521 | 160.1 | 1.780                 | 1.783                  | 12.3                |
| III-1   | C₄       | 2.485 | 158.3 | 1.782                 | 1.785                  | 28.0                |
| III-2   | C₄       | 2.498 | 157.8 | 1.783                 | 1.783                  | 89.1                |
| IV      | C₄       | 2.478 | 156.7 | 1.785                 | 1.785                  | 89.1                |
| I'      | C₄       | 2.707 | 166.6 | 1.717                 | 1.717                  | 89.9                |
| II'     | C₄       | 2.644 | 164.3 | 1.719                 | 1.719                  | 31.8                |
| III'    | C₃       | 2.615 | 163.0 | 1.720                 | 1.722                  | 24.9                |
| IV'     | C₃       | 2.623 | 161.5 | 1.722                 | 1.722                  |

Fig. 1 Optimized structures of the (a) F₂Mg···Y and (b) H₂Mg···Y [Y = CH₃, CH₂CH₃, CH(CH₃)₂, C(CH₃)₃] complexes and the relative energies of isomers (∆Eₑtot in kcal mol⁻¹) at the MP2/aug-cc-pVTZ level.
The singly occupied molecular orbitals (SOMOs) of the single-electron magnesium bonding orbitals energies (in eV) of the single-electron magnesium bonding complexes and corresponding monomers at the MP2/aug-cc-pVTZ level (see Fig. S2†). Herein, the Mg–C distance varies from 5.0 Å to 2.0 Å in steps of −0.3 Å, and the X–Mg–C angle increases from 90° to 102° with increments of 1.2°. As can be seen from the PES plot, the total energies of both dimers decrease as the MgX₂ molecule approaches the methyl radical, showing an attraction interaction between two species. Ultimately, minimum potential energy structures have been reached, which are basically consistent with the optimized structures of complexes I and I'. The singly occupied molecular orbitals (SOMOs) of the complexes and their corresponding free radicals are shown in Fig. 2. The singly occupied molecular orbitals and corresponding orbital energies (in eV) of the single-electron magnesium bonding complexes and corresponding monomers at the MP2/aug-cc-pVTZ level.

Table 2 NPA charges for the X₂Mg⋯Y [X = F, H; Y = CH₃, CH₂CH₃, CH(CH₂)₂, C(CH₃)₂] complexes at the MP2/aug-cc-pVTZ level (NPA charges are 1.863|e| and 0.932|e| for Mg and F atoms, respectively, in the MgF₂ monomer. NPA charges are 1.428|e| and −0.714|e| for Mg and H atoms, respectively, in the MgH₂ monomer).

| Complex | C₁ in monomer | In complex | Radial in complex | Mg in complex | Δq | X₁/X₂ in complex |
|---------|---------------|------------|-------------------|---------------|----|-----------------|
| I       | −0.467        | −0.527     | 0.019             | 1.842         | −0.021 | −0.931         |
| II-1    | −0.260        | −0.344     | 0.019             | 1.832         | −0.031 | −0.926         |
| II-2    | −0.347        | 0.018      | 0.018             | 1.841         | −0.022 | −0.931/−0.930  |
| III-1   | −0.072        | −0.165     | 0.015             | 1.835         | −0.028 | −0.926/−0.925  |
| III-2   | −0.166        | 0.018      | 0.018             | 1.833         | −0.030 | −0.925         |
| IV      | 0.102         | 0.011      | 0.004             | 1.844         | −0.019 | −0.924         |
| IV'     | −0.467        | −0.510     | 0.011             | 1.425         | −0.003 | −0.717         |
| IV''    | −0.260        | −0.323     | 0.011             | 1.429         | 0.001  | −0.720         |
| IV'''   | −0.072        | −0.140     | 0.012             | 1.433         | 0.005  | −0.720/−0.723  |
| IV''''  | 0.102         | 0.046      | 0.003             | 1.439         | 0.011  | −0.721         |

**Discussion**

The Mg–C binding distances (Å) for the MgF₂ and MgH₂ complexes are 2.573 and 2.707 Å, respectively, in the MgF₂ monomer. NPA charges are 1.428|e| and −0.714|e| for Mg and H atoms, respectively, in the MgH₂ monomer. The binding distances (Å), defined as the distance between Mg and C₁ atoms, are 2.573 and 2.707 Å for I and I', respectively. The interaction between F₂Mg and ethyl, isopropyl, and tertiary butyl results in five complexes. The II-1 and II-2 complexes can be regarded as being obtained when the H2 and H3 atoms of F₂Mg are replaced by methyl, respectively. The energy difference between them is only 0.02 kcal mol⁻¹. Similarly, the III-1 and III-2 isomers can be obtained when two of the methyl hydrogen atoms in F₂Mg⋯CH₃ are substituted. III-2 is 0.21 kcal mol⁻¹ higher in total energy relative to III-1. The situation is somewhat different for the BeH₂-based system. From Fig. 1, BeH₂ binding with ethyl (or isopropyl) leads to only one structure. It can be seen that isomer II' resembles II-1 in geometry, while the structure of III' parallels that of III-1. The F₂Mg⋯C(CH₃)₂ (IV) and H₂Mg⋯C(CH₃)₂ (IV') complexes share a similar geometry, and the [F₁MgC₁C₂ dihedral angle of 88.5° is close to the [H₁MgC₁C₂ dihedral angle of 88.9°.

Charges of the complexes and monomers are collected in Table 2. From Fig. 1 and Table 1, both F₂Mg⋯CH₃ (I) and H₂Mg⋯CH₃ (I') complexes possess C₃ symmetry. Their structural difference mainly comes from different interaction orientation between X₂Mg molecule and methyl, which is reflected in the ≪X1MgC1H1 dihedral angle (0° for I and 89.9° for I'). The binding distances (Å), defined as the distance between Mg and C₁ atoms, are 2.573 and 2.707 Å for I and I', respectively. The interaction between F₂Mg and ethyl, isopropyl, and tertiary butyl results in five complexes. The II-1 and II-2 complexes can be regarded as being obtained when the H2 and H3 atoms of F₂Mg are replaced by methyl, respectively. The energy difference between them is only 0.02 kcal mol⁻¹. Similarly, the III-1 and III-2 isomers can be obtained when two of the methyl hydrogen atoms in F₂Mg⋯CH₃ are substituted. III-2 is 0.21 kcal mol⁻¹ higher in total energy relative to III-1. The situation is somewhat different for the BeH₂-based system. From Fig. 1, MgH₂ binding with ethyl (or isopropyl) leads to only one structure. It can be seen that isomer II' resembles II-1 in geometry, while the structure of III' parallels that of III-1. The F₂Mg⋯C(CH₃)₂ (IV) and H₂Mg⋯C(CH₃)₂ (IV') complexes share a similar geometry, and the [F₁MgC₁C₂ dihedral angle of 88.5° is close to the [H₁MgC₁C₂ dihedral angle of 88.9°.

Besides, to evaluate the performance of modern DFT functionals for characterizing such magnesium-bonding system, structure optimizations of the X₂Mg⋯CH₃ and X₂Mg⋯CH₂CH₃ complexes were also performed by using the wb97 XD, M06-2X, B3LYP-D3(BJ), and B2LYP D3 methods with the aug-cc-pV TZ basis set. The results are compared with those of the MP2 method in Table S1 in ESL.† It can be found that all these DFT functionals tend to underestimate the Mg⋯C binding distance (by 0.034–0.156 Å). For the MgF₂-based system, the wb97 XD and M06-2X functionals overestimate the F–Mg–C angle while the other two underestimate it. For the MgH₂-based system, the H–Mg–C angle is always underestimated by these functionals. It is worth noting that the wb97 XD and M06-2X functionals can only yield the II-1 isomer, but fail to predict the II-2 isomer. In contrast, the B3LYP-D3(BJ) and B2LYP D3 functionals are able to predict both structures. Hence, it can be concluded that the B3LYP-D3(BJ) and B2LYP D3 methods can be used to describe the structures of the studied species and yield basically consistent results with those obtained at the MP2 level.

From Table 1, the binding distances of the studied X₂Mg⋯Y species vary in the range of 2.478–2.707 Å, which are far shorter than 3.9 Å, namely the sum of van der Waals radii of Mg and C atoms.† This fact indicates a certain interaction between MgF₂/MgH₂ and the radicals. To illustrate this, the potential energy surfaces of the F₂Mg⋯CH₃ and H₂Mg⋯CH₃ complexes have been roughly obtained by scanning the Mg⋯C distance and the X–Mg–C (X = F, H) angle at the MP2/aug-cc-pV TZ level (see Fig. S2†). Herein, the Mg⋯C distance varies from 5.0 Å to 2.0 Å in steps of −0.3 Å, and the X–Mg–C angle increases from 90° to 102° with increments of 1.2°. As can be seen from the PES plot, the total energies of both dimers decrease as the MgX₂ molecule approaches the methyl radical, showing an attraction interaction between two species. Ultimately, minimum potential energy structures have been reached, which are basically consistent with the optimized structures of complexes I and I'. The singly occupied molecular orbitals (SOMOs) of the complexes and their corresponding free radicals are shown in Fig. 2. The singly occupied molecular orbitals and corresponding orbital energies (in eV) of the single-electron magnesium bonding complexes and corresponding monomers at the MP2/aug-cc-pVTZ level.
To intuitively show the bonding between MgX₂ molecule and Y radicals, the independent gradient model (IGM) analysis of the X₂Mg···Y complexes was performed. A descriptor ($\Delta g^{\text{int}}$) is then derived that uniquely defines intermolecular interaction regions. The resulting $\Delta g^{\text{int}}$ isosurfaces are presented in Fig. 3. It is known that the blue and green colors on the isosurfaces stand for strong intermolecular attractive interaction and weak van der Waals interaction, respectively. As shown in Fig. 3, the single-electron Mg bond, which mainly lies between Mg and C₁ atoms, is represented by blue-green isosurfaces. Note that there are also small green regions between F of MgF₂ and methyl H atoms, is represented by blue-green isosurfaces. Note that there are also smaller green regions between F of MgF₂ and methyl H atom of the radicals in the II-2, III-1, III-2 and IV complexes, reflecting a weak intermolecular attraction. This can be understood given the relatively shorter F···H distances (2.706–2.762 Å) in these four dimers and the negative charge of the F atom (0.924–0.931$|\cdot\rangle$). The overall size of the isosurface increases as the number of methyl substituents increases, implying an increasing bonding strength. Note that the isosurfaces have more blue component for the F₂Mg···Y complexes compared with the H₂Mg-based series, indicating that the bonding strength of the former is stronger than that of the latter. This is consistent with the shorter L values of the former (2.478–2.573 Å) than those of the latter (2.623–2.707 Å).

From Table 1, the binding distance decreases in the sequence F₂Mg···CH₃ (2.573 Å) > F₂Mg···CH₂CH₃ (2.509 and 2.521 Å for II-I and II-2, respectively) > F₂Mg···CH(CH₃)₂ (2.485 and 2.498 Å for III-I and III-2, respectively) > F₂Mg···C(CH₃)₃ (2.478 Å). Hence, the methyl substitution effect on the formation of single-electron Mg bond is positive. Similarly, the Mg···C₁ distance of the H₂Mg-based series varies in the order H₂Mg···CH₃ (2.707 Å) > H₂Mg···CH₂CH₃ (2.644 Å) > H₂Mg···CH(CH₃)₂ (2.615 Å). Compared with H₂Mg···CH(CH₃)₃, the H₂Mg···C(CH₃)₃ complex has a slightly longer binding distance of 2.623 Å, which can be attributed to steric-hindrance effect. The case is similar to previously reported results of single-electron Be bonding systems.²⁸ Note that the Mg···X bond of MgX₂ is elongated by 0.010–0.017 Å upon the interaction with the Y radicals. Hence, the formation of single-electron Mg bond renders the Mg···X bonds weakened. In addition, the MgX₂ subunit bends from the linear geometry, and the bending angles ($\alpha$) are 156.7–166.6° (see Fig. 1 and Table 1). From Table 1, the more methyl groups the Y radical contains, the more the MgX₂ molecule is bent.

From natural population analysis (NPA), the Y moieties carry 0.003–0.019$|\cdot\rangle$ positive charges in the complexes (see Table 2), confirming that the radical plays the role of electron donor and MgX₂ serves as electron acceptor during the formation of single-electron Mg bond. To shed more light on the charge transfer interaction between MgF₂/MgH₂ and Y radicals, the related orbitals and corresponding second-order stabilization energies are listed in Table 3. For the F₂Mg-based series, the main charge transfer arises from the C₁ atom (LP(C)) of Mg to the empty s orbital (s*(Mg)) of Mg. For the F₂Mg···C(CH₃)₃ complex, there is an additional electron donation from LP(C) to the empty p orbital of Mg. As for the H₂Mg-based complexes, the LP(C) → p*(Mg) orbital interaction is dominant in intermolecular charge transfer. Besides, there are some minor charge transfer contributions, for example, from LP(C) to σ_MgH

| Complex | s*(Mg) → LP(C) | p*(Mg) → LP(C) | σ_MgH → p*(Mg) | σ_CH₁ | σ_CH₂ | σ_CH₃ | σ_CC |
|----------|----------------|----------------|----------------|--------|--------|--------|--------|
| I        | 20.11          | 9.34           | 19.08          | 13.82  | 9.30   | 14.37  | 2.47   |
| II-I     | 2.49           | 14.37          | 2.47/2.47      | 1.21   | 1.06   | 1.06   | 1.18   |
| II-2     | 13.82          | 2.33/2.33      | 1.38           | 1.38   |        |        |        |
| III-I    | 11.69          | 2.46/1.99      | 1.76           |        |        |        |        |
| III-2    | 8.88           | 1.90/1.90      |                |        |        |        |        |
antibonding orbital, from \( \sigma_{\text{CC}} \) bonding orbital to the empty 3s and 3\( p \) orbitals of Mg, and from the \( \sigma_{\text{CC}} \) bonding orbital to \( p^*(\text{Mg}) \) orbital (only for the IV' complex).

### 3.2 Interaction energies

Table 4 shows the interaction energies \( (E_{\text{int}}) \) of the studied single-electron magnesium bonding complexes. Clearly, basis set superposition error (BSSE) is not ignorable for interaction energy calculations. From the table, the BSSE values are 0.5–1.51 kcal mol\(^{-1} \) and 0.19–0.52 kcal mol\(^{-1} \) for the MgF\(_2\)- and MgH\(_2\)-based complexes, respectively. Besides, the BSSE values increase as the number of methyl groups in the radical increases and account for 9.7% and 5.5% of the CCSD(T) interaction energy for the MgF\(_2\)-\( \cdot \)C(CH\(_3\))\(_2\) and MgH\(_2\)-\( \cdot \)C(CH\(_3\))\(_2\) complexes, respectively. The MP2 interaction energies show a similar trend and close values to the CCSD(T) results, and their di

Table 5 LMOEDA partition terms (in kcal mol\(^{-1} \)) and the percentage contribution of electrostatic, polarization and dispersion components to the total attractive interaction energy for the X\(_2\)Mg\(_2\)-Y complexes:

| SCF | MP2 | CCSD(T) | BSSE | \( \rho(r) \) | \( \nabla^2 \rho(r) \) |
|-----|-----|---------|------|-------------|-----------------|
| I   | –7.04 | –7.48 | –6.81 | 0.04 | 0.14 | 0.06 |
| II-1 | –9.21 | –11.05 | –11.52 | 0.08 | 20.1% | 0.07 |
| II-2 | –9.48 | –11.18 | –11.70 | 0.81 | 19.0% | 0.06 |
| III-1 | –10.53 | –13.33 | –13.81 | 1.21 | 23.8% | 0.08 |
| III-2 | –10.90 | –13.52 | –14.06 | 1.09 | 22.5% | 0.07 |
| IV  | –11.36 | –15.12 | –15.36 | 1.51 | 27.0% | 0.09 |
| IV' | –3.62 | –6.94 | –7.13 | 0.30 | 40.2% | 0.03 |
| III' | –4.12 | –8.53 | –8.60 | 0.41 | 52.1% | 0.05 |
| IV' | –4.05 | –9.23 | –9.55 | 0.52 | 57.6% | 0.05 |

and 11.70 kcal mol\(^{-1} \) for II-1 and II-2, respectively) < F\(_2\)Mg\(_2\)-CH(CH\(_3\))\(_2\) (13.81 and 14.06 kcal mol\(^{-1} \) for III-1 and III-2, respectively) < F\(_2\)Mg\(_2\)-\( \cdot \)C(CH\(_3\))\(_2\) (15.56 kcal mol\(^{-1} \)). This trend also applies to the MgH\(_2\)-based series. Obviously, the interaction energy of an X\(_2\)Mg\(_2\)-alkyl complex becomes larger as more methyl substituents are involved in the alkyl radical. Note that the interaction energy of isomer II-2 is 0.18 kcal mol\(^{-1} \) larger than that of II-1, which might be attributed to the additional F\(^2\)-H\(^2\) interaction in II-2. Similarly, isomer III-2 contains one more F\(^2\)-H\(^2\) secondary interaction compared with III-1, justifying its slightly larger interaction energy.

From Table 4, the interaction energies vary from –8.61 to –15.56 kcal mol\(^{-1} \) for the F\(_2\)Mg\(_2\)-Y complexes, and from –5.25 to –9.55 kcal mol\(^{-1} \) for the H\(_2\)Mg\(_2\)-Y series. Note that these values are comparable to those (–6.13 to –14.92 kcal mol\(^{-1} \))\(^{89} \) of the X\(_2\)Be\(_2\)-Y [X = F, H; Y = CH\(_3\), CH\(_2\)CH\(_3\), CH(CH\(_3\))\(_2\), and C(CH\(_3\))\(_3\)] complexes. Meanwhile, the interaction energies are –13.47 ~ –15.80 kcal mol\(^{-1} \) for F\(_2\)Mg\(_2\)-\( \pi \) and ~7.22 ~ –8.91 kcal mol\(^{-1} \) for H\(_2\)Mg\(_2\)-\( \pi \) interactions where the \( \pi \) electron donors are acetylene, ethylene and benzene molecules.\(^{86} \) Hence, it can be concluded that single-electron magnesium bond, single-electron beryllium bond, and \( \pi \)-magnesium bond are comparable in strength.

To deepen the understanding of the nature of single-electron Mg bond, the interaction energies of the X\(_2\)Mg\(_2\)-Y complexes have been further analyzed by using the LMOEDA method. The energy decomposition results present considerable electrostatic and polarization interactions in the complexation between MgX\(_2\) and radical molecules. The former accounts for approximately half of the total attractive interaction energy, and the latter makes up 27.6–38.1% (see Table 5). Besides, the dispersion energy contributes 5.7–21.6% to the stabilization of the studied complexes, especially for the MgH\(_2\)-based series. From the table, all the terms, namely the electrostatic, polarization, exchange-repulsion and dispersion energies, increase with the growth of number of methyl groups in the system except that III-2 has a slightly higher electrostatic energy than IV. The LMOEDA analysis also reveals that a F\(_2\)Mg\(_2\)-Y complex possesses larger attractive interaction energy and smaller
exchange-repulsion energy than corresponding \( \text{H}_2\text{Mg} \cdots \text{Y} \) complex, giving rise to the larger \( E_{\text{int}} \) value of the former.

### 3.3 Harmonic vibrational frequencies

Main harmonic vibrational frequencies and their corresponding infrared intensities of the \( \text{X}_2\text{Mg} \cdots \text{Y} \) complexes are shown in Table 6. From the table, the magnesium bond stretching vibration of the \( \text{F}_2\text{Mg} \cdots \text{Y} \) complexes occurs in the 200.8–258.5 cm\(^{-1}\) region, comparable to that of 208.0–240.7 cm\(^{-1}\) for the \( \text{F}_2\text{Mg} \cdots \pi \) bonding species.\(^{36} \) The \( \text{Mg} \cdots \text{C} \) stretching vibrational frequency of the \( \text{H}_2\text{Mg} \cdots \text{Y} \) series, on the other hand, shows an apparent increase as more methyl groups are involved in the electron donor.

From Table 6, both \( \text{X} \cdots \text{Mg} \cdots \text{X} \) symmetric and antisymmetric stretching vibrational frequencies decrease as a result of the complexation between \( \text{MgX}_2 \) and radical molecules, which accords well with the lengthening of the \( \text{Mg} \cdots \text{X} \) bonds. The antisymmetric \( \text{X} \cdots \text{Mg} \cdots \text{X} \) and symmetric \( \text{H} \cdots \text{Mg} \cdots \text{H} \) stretching vibration frequencies are red-shifted by 30.7 to 56.3 cm\(^{-1}\) in the complexes. In contrast, the \( \text{F} \cdots \text{Mg} \cdots \text{F} \) symmetric stretching frequency has a minor redshift of less than 10 cm\(^{-1}\). This may be attributed to the stronger intermolecular interaction of the \( \text{F}_2\text{Mg} \cdots \text{Y} \) complexes and the bent structure of the \( \text{MgF}_2 \) subunit, which bring about coupling of the symmetric stretch of the \( \text{F} \cdots \text{Mg} \cdots \text{F} \) bond with the stretching \( \text{Mg} \cdots \text{C} \) bond. Note that the similar vibrational-mode coupling even results in abnormal blue-shifted \( \text{F} \cdots \text{Be} \cdots \text{F} \) symmetric stretch in the studies of beryllium bonding systems.\(^{34,58} \) In addition, it has been found that the antisymmetric stretching vibration of the \( \text{MgX}_2 \) subunit has larger IR intensity than symmetric stretching vibration, especially in the \( \text{MgH}_2 \)-based complexes.

### 3.4 AIM analysis

Bader’s quantum theory of atoms in molecules (QTAIM) was applied to the topic complexes to gain more insight into the nature of single-electron magnesium bond. The electron

| \( \text{v} \) in complex | \( \Delta \text{v} \) | IR intensity | \( \text{v} \) in complex | \( \Delta \text{v} \) | IR intensity | Mg \cdots C stretch \( \nu \) |
|---|---|---|---|---|---|---|
| I | 544.7 | -6.8 | 17.4 | 830.6 | -30.7 | 152.5 | 209.5 |
| II-1 | 544.1 | -7.4 | 24.3 | 825.0 | -36.3 | 96.0 | 229.2 |
| II-2 | 543.6 | -7.9 | 25.0 | 822.4 | -38.9 | 146.5 | 224.5 |
| III-1 | 542.5 | -9.0 | 31.5 | 815.7 | -45.6 | 140.3 | 258.5 |
| III-2 | 543.2 | -8.3 | 32.1 | 815.5 | -45.8 | 142.5 | 249.7 |
| IV | 541.7 | -9.8 | 34.2 | 809.9 | -51.4 | 134.4 | 200.8 |
| IV' | 1601.9 | -34.3 | 13.4 | 1621.0 | -38.0 | 484.3 | 150.4 |
| III' | 1594.7 | -41.5 | 21.7 | 1612.5 | -46.5 | 485.3 | 173.3 |
| IV' | 1588.7 | -47.5 | 33.6 | 1606.5 | -52.5 | 473.0 | 231.9 |
| IV'' | 1586.1 | -50.1 | 38.1 | 1602.7 | -56.3 | 465.6 | 352.8 |
densities (ρ) and their Laplacians (∇²ρ) at the Mg···C1 bond critical points (BCPs) have been obtained, which are listed in Table 4. The molecular graphs of the complexes are presented in Fig. 4.

From Fig. 4, there are bond critical points between MgX₂ and radicals in all the cases, indicating the formation of single-electron magnesium bond therein. It is worth mentioning that there are also interaction paths between F of MgF₂ and H of the C(CH₃)₃ radical in complex IV, only their corresponding electron density (ρ = 0.006 au.) is quite small. As shown in Table 4, the values of electron density and Laplacians at the Mg···C1 BCPs are in the range of 0.012–0.019 and 0.039–0.084 au, respectively. Besides, both ρ and ∇²ρ values increase gradually with the increasing number of methyl groups involved in the X₂Mg···Y complexes. From Fig. S3b,† the evolution of electron density at the Mg···C1 BCP shows a similar trend to that of interaction energy. This again reflects the positive role of the methyl substituent in the single-electron magnesium bond formation. According to a previous study of π-magnesium bond, the values of electron density at the π···Mg BCPs also range from 0.012 to 0.019 au.,** also reflecting that π-magnesium bond and single-electron magnesium bond are close to each other in strength.

4. Conclusions

According to quantum chemical calculations, the MgX₂ (X = F, H) molecules are able to serve as Lewis acids and form complexes with alkyl radicals [Y = CH₃, CH₂CH₃, CH(CH₃)₂, and C(CH₃)₃]. The existence of single-electron magnesium bond is thereby proposed. Upon the interaction with radicals, the MgX₂ molecule becomes bent, accompanied by elongated Mg–X bonds and red-shifted X–Mg–X stretching vibrations. LMOEDA analysis demonstrates that the electrostatic and polarization interactions make dominant contributions to the stability of the topic complexes. Besides, there is 0.003–0.019|e| electron transfer from the radical molecules to MgX₂ during complexation and the main electron donation takes place from the SOMO orbital of the radicals to the 3s or 3p orbital of Mg. It has been found that, the more methyl groups are involved in electron donor Y, the shorter the binding distance and the larger the interaction energy of the X₂Mg···Y complex, showing the positive effect of methyl substitution on single-electron magnesium bonding formation. We hope that the results of this study can further enrich the knowledge of intermolecular weak interactions, and may provide meaningful references for biological and chemical processes that involve radicals.

Conflicts of interest

There are no conflicts to declare.

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