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# Cooperative and Diminutive Interplay between Halogen, Hydride and Cation-σ Interactions

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In the present study, the cooperative and diminutive interplay between halogen, hydride, and cation-σ interactions are studied in HMgH···$Li^+$($Na^+$)···NCCl, $Li^+$($Na^+$)···HMgH···ClCN and HMgH···ClCN···$Li^+$($Na^+$) complexes by means of *ab initio* calculations. To better understand the cooperative or diminutive effects in the ternary systems, the corresponding binary complexes are also considered. The estimated cooperative energies ($E_{coop}$) are all negative for the systems with CNCl in the central location, while positive in the other systems. In addition, complexes involving cation-σ interactions have the largest stability energy among studied complexes. The electronic properties of the complexes are analyzed using parameters derived from the quantum theory of atoms in molecules methodology.

**Keywords:** Cation-σ interactions, Cooperative, Diminutive, Many-body interaction energy

## INTRODUCTION

Noncovalent interactions between molecules play a very important role in supramolecular chemistry, molecular biology, and materials science [1-5]. Halogen bond [6,7] and hydride bond [8-10] are two important types of noncovalent interactions. A halogen bond is usually formulated as A-X···B interaction, in which the halogen atom (X), acts as a bridge to an electron-rich site of the Lewis base (B). There have been numerous experimental and theoretical studies about the practical and potential applications of halogen bonds in various fields of supramolecular chemistry and biochemistry [10, 11-18].

In the other hand, the interaction between alkaline metals and hydride compounds is important for an innovative research [19,20]. The hydride compound considered in the present study, $MgH_2$, is of primary importance for experimental studies and has been proposed as a potential hydrogen storage material [21,22].

According to our knowledge, a hetero atom is able to form cation-σ interactions by donating its lone pair to the cation. This interaction is consequential, due to its ability to be discussed in comparison with cation-π binding [23] and some other interactions as our work. Cooperative or diminutive effects involving halogen bond, hydride bond and cation-σ interactions are very interesting due to their extremely importance in chemical reactions and regulation of biochemical process.

The cooperative effect is observed for ternary systems when the central moiety acts as Lewis acid and Lewis base, simultaneously [24], as HMgH···ClCN···$Li^+$($Na^+$) system in our work. Also the ternary systems with central moiety acting as either the Lewis acid or Lewis base, exhibit a diminutive effect because of electron density accepting or donating from both sides [24]. So, it is expected that the interactions containing cation or HMgH in the central position, as some systems in the present work, have a diminutive energy.

In this study, the interplay interaction between the

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*Corresponding author. E-mail: m-solimannejad@araku.ac.ir hydride bond and cation-σ as $HMgH\cdots Li^{+}(Na^{+})\cdots NCCl$, hydride bond and halogen bond as $Li^{+}(Na^{+})\cdots HMgH\cdots ClCN$, halogen bond and cation-σ as $HMgH\cdots ClCN\cdots Li^{+}(Na^{+})$ in ternary complexes are investigated by means of *ab initio* calculations. To the best of our knowledge, this is the first study which reports the cooperative, diminutive and many-body interaction analyses for these designed triads.

## COMPUTATIONAL DETAILS

The geometries of all monomers, dimers and trimers were optimized at the MP2/aug-cc-pVDZ computational level using the Gaussian 09 system of codes [25]. The stabilization energies of all optimized complexes were obtained at the same level. They have been computed as the differences between the total energies of the complexes and the energies of the isolated monomers at their energy minima and were corrected for basis set superposition error (BSSE) using the counterpoise method [26]. The electron densities of the isolated molecules and complexes were analyzed using the quantum theory of atoms in molecules (QTAIM) methodology [27].

## RESULTS AND DISCUSSION

### Monomers

The molecular electrostatic potential (MEP) of the isolated ClCN and $MgH_2$ molecules (Fig. 1) shows negative regions at the terminal positions, N side in ClCN and H sides in $MgH_2$, and positive regions at the Cl and Mg side.

### Geometries

The systems studied form stable triads with $C_{\infty V}$ symmetry. The bond angle between monomers within triad complexes is 180º and all studied triads have a linear structure. It should be noted that T-shape structures with the interaction aligned in the carbon of ClCN were also optimized but the optimized structures have all negative frequencies, so, T-shape structures are not local minima and not considered for more analysis.

According to values presented in Table 1, all binding distances in the arrangement of diminutive triads are longer than the corresponding values in the dyads, while those of in cooperative triads are shorter.

Furthermore, comparison of the binding distances indicates that $H\cdots Li^{+}(Na^{+})$ distances difference ($\Delta R_{AB}$) in $HMgH\cdots Li^{+}(Na^{+})\cdots NCCl$ arrangement are larger than the correspond values in $Li^{+}(Na^{+})\cdots HMgH\cdots ClCN$. This indicates that the presence of a cation-σ interaction in the ternary systems with first mentioned arrangement affects on $\Delta R_{AB}$, that is reported here for the first time.

### Energy Analysis

The values of the BSSE-corrected stabilization energy of dyads SE(AB), SE(BC) and triads SE(ABC), obtained using Eqs. (1) and (2), are listed in Table 2. In these equations, $E_{AB}$ and $E_{ABC}$ are the total electronic energy of the dimer and trimer. $E_A$, $E_B$ and $E_C$ are the total electronic energy of the isolated monomers within their corresponding minima configuration. All results were corrected for the BSSE.

$$SE(AB) = E_{AB} - (E_A + E_B) + BSSE_{AB} \qquad (1)$$

$$SE(ABC) = E_{ABC} - (E_A + E_B + E_C) + BSSE_{ABC} \qquad (2)$$

As shown in Table 2, the ternary systems with cation in central position have the largest stabilization energy among the studied triads. Also, all of binary and ternary systems containing $Li^{+}$ have larger stabilization energy values compared to systems containing $Na^{+}$. As another finding, binary and ternary complexes involving cation-σ interaction ($Li^{+}\cdots N$, $Na^{+}\cdots N$) have a larger stability energy than other complexes.

Then, an energetic cooperativity parameter was calculated using the following equation [28,29]:

$$E_{coop} = SE(ABC) - SE(AB) - SE(BC) - E_i(AC) \qquad (3)$$

where $E_i(AC)$ is the interaction energy of the imaginary system involving A and C monomers frozen in the geometry of triads.

In the studied complexes, cooperative effects are seen for the ternary systems involving NCCl molecule in the middle position due to its dual role as Lewis acid and Lewis base. As shown in the MEP of ClCN, the negative and positive regions show the dual role of ClCN as electron donor (lone pairs of N) and electron accepting (σ-hole on

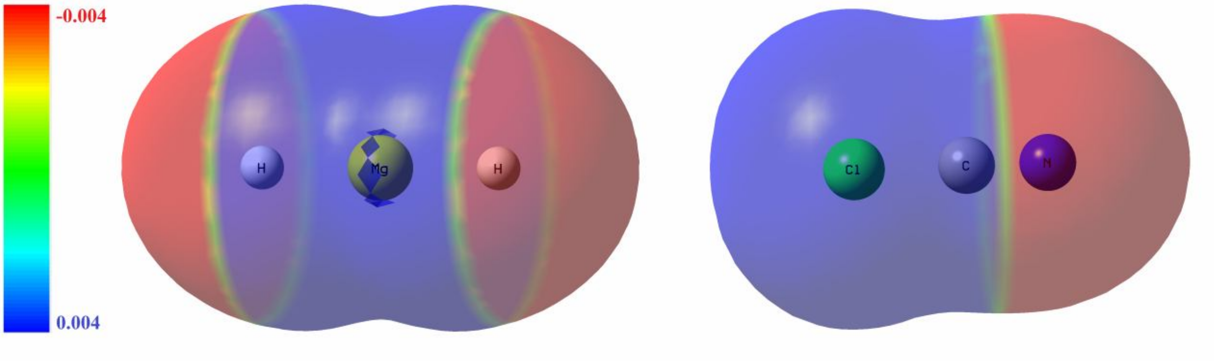

**Fig. 1.** Representation of the MEP in the isolated $MgH_2$ and ClCN monomers at ±0.004 a.u. isosurface. Negative regions are represented in red, and positive ones are in blue.

**Table 1.** Intermolecular Distances R (Å) in the Investigated Triads (T), and Dyads. ΔR Indicates the Changes Relative to Respective Dyads

| Triads(A···B···C) | R(AB,T) | R(AB) | $\Delta R_{AB}$ | R(BC,T) | R(BC) | $\Delta R_{BC}$ |
|---|---|---|---|---|---|---|
| HMgH···$Li^+$···NCCl | 1.745 | 1.722 | 0.023 | 1.989 | 1.961 | 0.028 |
| HMgH···$Na^+$···NCCl | 2.130 | 2.104 | 0.026 | 2.371 | 2.343 | 0.028 |
| $Li^+$···HMgH···ClCN | 1.728 | 1.722 | 0.006 | 2.920 | 2.720 | 0.200 |
| $Na^+$···HMgH···ClCN | 2.115 | 2.104 | 0.011 | 2.886 | 2.720 | 0.166 |
| HMgH···ClCN···$Li^+$ | 2.476 | 2.720 | -0.244 | 1.943 | 1.961 | -0.018 |
| HMgH···ClCN···$Na^+$ | 2.516 | 2.720 | -0.204 | 2.323 | 2.343 | -0.020 |

**Table 2.** Stabilization Energies SE (kJ $mol^{-1}$) of the Studied Dyads and Triads at MP2/aug-cc-pvdz Level

| Triads(A···B···C) | SE(ABC) | SE(AB) | SE(BC) | $E_{coop}$ |
|---|---|---|---|---|
| $MgH_2$···$Li^+$···NCCl | -251.57 | -128.30 | -145.71 | 22.44 |
| $MgH_2$···$Na^+$···NCCl | -177.49 | -87.21 | -102.65 | 12.37 |
| $Li^+$···HMgH···ClCN | -124.47 | -128.30 | -10.89 | 14.71 |
| $Na^+$···HMgH···ClCN | -84.61 | -87.21 | -10.89 | 13.49 |
| HMgH···ClCN···$Li^+$ | -175.77 | -10.89 | -145.71 | -19.18 |
| HMgH···ClCN···$Na^+$ | -129.10 | -10.89 | -102.65 | -15.57 |

Cl). In the same way, diminutive effects are observed for complexes with $MgH_2$ or cation in the central position, in the range between 13.49-22.44 kJ mol$^{-1}$. These results show that the cooperative energies are mainly dependent on the position of the monomers in the triad arrangement [24].

## Many-Body Interaction Analysis

The two-body terms ($\Delta E^2_{A\text{-}B}$, $\Delta E^2_{B\text{-}C}$ and $\Delta E^2_{A\text{-}C}$) can be calculated as the difference between the total energy of each molecular pair in the geometry of triad and sum of the isolated monomers, all of which are frozen in the geometry of the triad (see Eq. (4)) [30-32]. The three-body term $\Delta E^3_{A\text{-}B\text{-}C}$ is defined as Eq. (5), which can be regarded as a measure of cooperative or diminutive effects in a three-body system [30-32].

$$\Delta E^2_{A\text{-}B} = E_{AB} - (E_A + E_B) \tag{4}$$

$$\Delta E^3_{A\text{-}B\text{-}C} = E_{ABC} - (E_A + E_B + E_C) - \Delta E^2_{A\text{-}B} - \Delta E^2_{B\text{-}C} - \Delta E^2_{A\text{-}C} \tag{5}$$

The strain energy ($E_S$) is described as the energy sum of the monomers frozen in the geometry of triads minus the energy sum of the optimized monomers. Thus, the total binding energy of the triad is obtained using Eq. (6):

$$SE(ABC) = \Delta E^2_{A\text{-}B} + \Delta E^2_{B\text{-}C} + \Delta E^2_{A\text{-}C} + \Delta E^3_{A\text{-}B\text{-}C} + E_S \tag{6}$$

The results in Table 3 show that the main contribution of stabilization energies is obtained by the two-body interaction term in this order: $\Delta E^2_{\text{cation-}\sigma} > \Delta E^2_{\text{hydride bond}} > \Delta E^2_{\text{halogen bond}}$. This means that cation-σ bonds and halogen bonds have the largest and the least contribution into the bonding interaction between two molecules in a triad, respectively.

In the all studied systems, the two-body $\Delta E^2_{A\text{-}C}$ and three-body $\Delta E^3_{A\text{-}B\text{-}C}$ interaction energy terms have negative values (attractive) for cooperative triads and positive values (repulsive) for diminutive triads. Due to the large distance between the interacting molecules A and C of the corresponding triads $\Delta E^2_{A\text{-}C}$ is the smallest two-body interaction term for all triads.

The strain energy ($E_S$) can be defined as a measure of the degree of strain that drives the distortion of the ternary system. Equation (7) describes how calculate the $E_S$. As seen in Eq. (7), $E_S$ calculated by sum of the monomers energies frozen in the geometry of the triads minus the energy sum of the optimized monomers.

$$E_S = (E_A + E_B + E_C)_T - (E_A + E_B + E_C) \tag{7}$$

As seen in Table 3, the strain energy is positive, that causes a destabilizing contribution to the total stabilization energy of the triads.

## Electron Density Analysis

As one of the aims of the present study, the QTAIM topological parameters were used to analyze the characteristics of the hydride bond, cation-σ and halogen bond interactions through the location of the corresponding bond critical point (BCP). The changes in QTAIM parameters, namely as the variations in electron density ($\Delta\rho$) and the Laplacian of electron density ($\Delta\nabla^2\rho$) are summarized in Table 4. Molecular graph of the studied triads are shown in Supplementary Data.

The values of the electron density in the intermolecular BCPs show a clear dependency on the interatomic distance. In addition, increasing and decreasing in electron density and Laplacian of electron density are observed for the cooperative and diminutive triads, respectively, upon the triad formation. A good linear relationship was found between the $E_{coop}$ and $\Delta\rho_{A\text{-}B}$ values as indicated in Eq. (8) and Fig. 2:

$$E_{coop} = -4839.3\Delta\rho_{A\text{-}B} - 4.2563, \qquad R^2 = 0.97 \tag{8}$$

# CONCLUSIONS

In the present study, some factors affecting the bonding properties, such as the nature of the cation and arrangement of the interacting molecules were investigated in the ternary $HMgH\cdots Li^+(Na^+)\cdots NCCl$, $Li^+(Na^+)\cdots HMgH\cdots ClCN$ and $HMgH\cdots ClCN\cdots Li^+(Na^+)$ complexes. The triads with $Li^+$ showed large absolute cooperative values compared with the similar triads containing $Na^+$. Systems involving cation-σ interactions have the largest stability energy among the studied complexes. The cooperative effect was observed in

**Table 3.** Decomposition of Stabilization Energy (kJ mol$^{-1}$) of the Studied Triads

| Triads(A$\cdots$B$\cdots$C) | $\Delta E^2_{A-B}$ | $\Delta E^2_{B-C}$ | $\Delta E^2_{A-C}$ | $\Delta E^3_{A-B-C}$ | $E_S$ |
|---|---|---|---|---|---|
| $MgH_2\cdots Li^+\cdots NCCl$ | -129.43 | -146.64 | 4.13 | 17.99 | 2.38 |
| $MgH_2\cdots Na^+\cdots NCCl$ | -88.26 | -103.23 | 2.67 | 9.54 | 1.80 |
| $Li^+\cdots HMgH\cdots ClCN$ | -130.18 | -10.31 | 8.51 | 5.60 | 1.90 |
| $Na^+\cdots HMgH\cdots ClCN$ | -88.52 | -10.47 | 7.95 | 5.10 | 1.34 |
| $HMgH\cdots ClCN\cdots Li^+$ | -8.74 | -146.11 | -6.53 | -15.66 | 1.00 |
| $HMgH\cdots ClCN\cdots Na^+$ | -9.21 | -102.83 | -5.61 | -12.08 | 0.63 |

**Table 4.** Changes in QTAIM Parameters of the Triads Relative to the Respective Dyads

| Triads(A$\cdots$B$\cdots$C) | $\Delta\rho_{A-B}$ | $\Delta\nabla^2\rho_{A-B}$ | $\Delta\rho_{B-C}$ | $\Delta\nabla^2\rho_{B-C}$ |
|---|---|---|---|---|
| $MgH_2\cdots Li^+\cdots NCCl$ | -0.0014 | -0.0109 | -0.0019 | -0.0209 |
| $MgH_2\cdots Na^+\cdots NCCl$ | -0.0012 | -0.0056 | -0.0015 | -0.0119 |
| $Li^+\cdots HMgH\cdots ClCN$ | -0.0003 | -0.0018 | -0.0036 | -0.0103 |
| $Na^+\cdots HMgH\cdots ClCN$ | -0.0005 | -0.0025 | -0.0031 | -0.0087 |
| $HMgH\cdots ClCN\cdots Li^+$ | 0.0066 | 0.0149 | 0.0016 | 0.0137 |
| $HMgH\cdots ClCN\cdots Na^+$ | 0.0053 | 0.0123 | 0.0012 | 0.0089 |

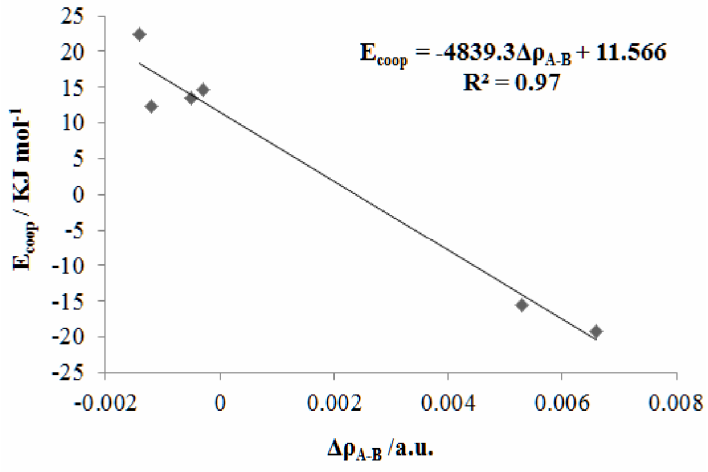

**Fig. 2.** $E_{coop}$ *vs.* $\Delta\rho_{A-B}$.

HMgH⋯ClCN⋯$Li^+$($Na^+$) system, while $MgH_2$⋯ $Li^+$($Na^+$)⋯NCCl and $Li^+$($Na^+$)⋯HMgH⋯ClCN systems have a diminutive effect. We hope that the results of the present study could be useful for understanding the cooperative and competitive role of halogen, hydride and cation-σ bond interactions in biological systems, molecular recognizing and crystal engineering.

## Supplementary Data

Molecular graph of the studied triads at the MP2/aug-cc-pvDZ level and Cartesian coordinates of the optimized triads at the MP2/aug-cc-pvDZ level.

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