Insight into Spodium–π Bonding Characteristics of the MX₂···π (M = Zn, Cd and Hg; X = Cl, Br and I) Complexes—A Theoretical Study

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Abstract: The spodium–π bonding between MX₂ (M = Zn, Cd, and Hg; X = Cl, Br, and I) acting as a Lewis acid, and C₂H₂/C₂H₄ acting as a Lewis base was studied by ab initio calculations. Two types of structures of cross (T) and parallel (P) forms are obtained. For the T form, the X–M–X axis adopts a cross configuration with the molecular axis of C≡C or C=C, but both of them are parallel in the P form. NCI, AIM, and electron density shifts analyses further, indicating that the spodium–π bonding exists in the binary complexes. Spodium–π bonding exhibits a partially covalent nature characterized with a negative energy density and large interaction energy. With the increase of electronegativity of the substituents on the Lewis acid or its decrease in the Lewis base, the interaction energies increase and vice versa. The spodium–π interaction is dominated by electrostatic interaction in most complexes, whereas dispersion and electrostatic energies are responsible for the stability of the MX₂···C₂F₂ complexes. The spodium–π bonding further complements the concept of the spodium bond and provides a wider range of research on the adjustment of the strength of spodium bond.

Keywords: spodium–π bonding; substituent effect; NCI; AIM; electron density shift

1. Introduction

Spodium bond (SpB) [1] refers to the net attractive interaction between a Group 12 element and an electron-rich atom. SpB plays a crucial role in supramolecular chemistry [2–7] and crystal engineering [8,9]. For example, a 2D supramolecular polymeric of [Hg₂L(N₃)₁]₄P₃, prepared with Hg(CH₃COO)₂, NaN₃, and 1,2-bis(pyridin-2-ylmethylene)hydrazine, non-covalent interactions, including spodium bonding, have a defining structure-guiding role. Two new dinuclear Zn(II) complexes [5] were synthesized and characterized. By using a combination of Bader’s quantum theory of “atoms in molecules” (QTAIM) and noncovalent interaction (NCI) method analyses, intramolecular SpBs were characterized and differentiated from coordination bonds [5]. What is more, there is already evidence on the existence and relevance of SpB in biological systems [10,11]. The evidence of spodium bonds in tetrahedral Zn-binding sites [10] demonstrates that Zn SpB’s are abundant and might be involved in protein structures and enzyme inhibition. The strength of three protein models’ SpB interactions in biologically relevant metalloenzymes [11] was estimated by using a combination of QTAIM and NCI plot index computational tools.

After the concept of SpB was proposed, the related experimental and theoretical studies were reported rapidly [12–22]. The non-covalent SpB between the tetracoordinated molecules MX₂L₂ (M = Zn, Cd, Hg; X = Cl, Br, I; L = thiourea) and the electron-donating molecules is different from the coordination bonds (anti-bonding Sp–ligand orbital involved). The HgCl₂···L dimers (where L = CIR, SR₂, PR₃ families) were explored to unveil
the nature of the linear coordinated spodium bonds [12]. In addition, the ability of the HgX$_2$ (X = Cl, Br, I) dimer to establish secondary Hg···X contacts (spodium bond) and Hg···Hg was described [9,13]. The structures, intermolecular interactions, and the spectral variations in the mixtures containing a wide range of compositions (1:3 to 1:14 in molar ratios) of ethanol and ZnCl$_2$ was explored to shed light on understanding the properties of the deep eutectic solvents formed by them [14]. What is more, the bi-coordinated molecules ZnX$_2$ interact with either a carbene [15,16] or carbodiphosphorane [15] carbon atom, resulting in a C···Zn bond. Compared with the beryllium bond, the C···Zn bond is not much different than the beryllium bond, and both have a significant covalent contribution [15]. The planar MCl$_3^−$ (M = Zn, Cd, Hg) anions containing a negative $\pi$-hole region form a complex with the CN$^−$ anion [17] or one another MX$_3^−$ [18,19]. The anion···anion spodium bonds and crystal packing forces attribute to some crystal structures [18]. In addition, the SpB coexists simultaneously with other non-covalent interactions in the same system. For example, Liu et al. explored the cooperativity between SpB and pnicogen [20]/chalcogen [21]/tetrel bonds [22] in ternary complexes, and these interactions are strengthened by each other. Accordingly, the electron donors are lone pair electrons and carbones.

Usually, the $\pi$ system (ethyne and ethene) is one the candidate electron donor and participates in the $\sigma/\pi$-hole interactions [23–25], such as the aerogen bond [24], hydrogen bond [26–30], lithium bond [31–33], beryllium bond [34], sodium bond [35], magnesium bond [36], regium bond [37–40], triel bond [41], tetrel bond [42,43], pnictogen bond [44], chalcogen bond [45], halogen bond [46], and so on [47–49]. Wang et al. [50] provided some experimental evidence for the zinc–diborene $\pi$ interactions in complexes of Zn(II)/Cd(II) with diborene. However, there is no theoretical research on the spodium bonds involved in $\pi$ systems.

Hence, in this paper, we first study the interaction between MX$_2$ (M=Zn, Cd, and Hg; X = Cl, Br, and I) and C$_2$H$_2$/C$_2$H$_4$ to explore the dependence of spodium bonding strength on the nature of the M atom and the hybridization of $\pi$ molecular as well as to unveil the origin of a spodium bond. MX$_2$ is a well-known linear molecule which has a large positive electrostatic potential generated on the waist of the Group 12 atom. C$_2$H$_2$ and C$_2$H$_4$ have a negative electrostatic potential region above and below the C=C/C≡C. Thus, there should be a strong attraction interaction between them. Considering the stronger electron-withdrawing ability of the F atom and the stronger electron-donating ability of the Li atom, the H atoms in C$_2$H$_2$ are replaced with –F and –Li, and the corresponding systems were used to study substitution effects on the interactions. What is more, we utilize $sp$-hybridized C$_2$H$_2$ and $sp^2$-hybridized C$_2$H$_4$ interacted with MX$_2$ to explore the hybridization effect.

2. Theoretical Methods

The second-order Möller–Plesset (MP2) perturbation theory [51] has been a good method for studying intermolecular interactions [24,39,52–56]. Furthermore, the MP2 method was adopted to study spodium bonds [1,18,20,21]. All complexes were optimized using MP2 perturbation theory with aug-cc-pVTZ basis sets [57,58]. Moreover, for iodine, zinc, chromium, and mercury atoms, the aug-cc-pVTZ-PP basis set was adopted to account for relativistic effects. Two types of structures of the cross (T) and parallel (P) forms were obtained. The frequency analysis at the same computational level was applied to affirm that the optimized geometries corresponded to the ground-state stationary points. It is worth noting that for ethyne and ethene complexes, the global minima corresponded to the P form, while the T form was a transition state with 1 imaginary frequency. The interaction energy was defined as the difference between the energy of the complex and the energies of the monomers with their geometries taken from the complex. Using the counterpoise method proposed by Boys and Bernardi [59], the interaction energy was corrected for the basis set superposition error (BSSE). All calculations were performed using Gaussian 09 package [60]. The interaction energy was also analyzed at the MP2/aug-cc-pVTZ (PP) level by the localized molecular orbital energy decomposition analysis (LMOEDA) method [61] with GAMESS program [62]. The total interaction energy can be decomposed
into 5 components: electrostatic (ES); exchange (EX); repulsion (REP); polarization (POL); and dispersion (DISP) energies.

Molecular electrostatic potentials (MEPs) on the 0.001 electrons bohr$^{-3}$ contour of the electronic density were calculated with the Multiwfn [63] at the MP2/aug-cc-pVTZ(PP) level. To obtain a deeper insight into the interaction nature of these complexes in the light of charge transfer and orbital interactions, we performed natural bond orbital (NBO) [64] analyses included in Gaussian 09. Quantum theory of “atoms in molecules” (QTAIM) analysis [65] was performed with the Multiwfn [63] to obtain topological parameters of the bond critical point (BCP), including electron density ($\rho$), its Laplacian ($\nabla^2 \rho$), and total energy density ($H$). Since the electron density is at a maximum at the nuclei, the localization of maxima enables the identification of atomic positions. The first-order saddle points between the maxima are usually known as bond critical points (BCPs) [34,65]. The wavefunctions were used to perform topological analyses for these complexes, including non-covalent interaction (NCI). NCI maps were plotted with the VMD program [66]. NCI involves the reduced density gradient (RDG) and the electron density ($\rho$). RDG is defined as:

$$\text{RDG} = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho|}{\rho^{4/3}},$$

3. Results and Discussion

3.1. Molecular Electrostatic Potential of Monomers

Molecular electrostatic potential (MEP) is a very effective method for predicting the possibility of intermolecular interactions, which could ascertain the most appropriate interaction region of each monomer [12,20,67–69]. Figure 1 depicts the MEP maps of ZnBr$_2$ and $\pi$ systems. It is evident that the most positive MEP ($V_{\text{max}}$) was generated on the waist of Zn atom in ZnBr$_2$, which was similar to the rest of the MX$_2$ monomers ($M = Zn$, Cd, Hg; $X=Cl$, Br, I), and the most negative MEP ($V_{\text{min}}$) was between two carbons in the $\pi$ systems. There should be a strong attraction between the M atom and a $\pi$ system. The values of $V_{\text{max}}$ and $V_{\text{min}}$ for monomers are collected in Table 1. It is immediate that for the MX$_2$ with the same M and different halogen atoms, the value of $V_{\text{max}}$ on the M atom increased in the order of I < Br < Cl; and for the ones with the same halogen atom, $V_{\text{max}}$ became more positive in the order of Hg < Zn < Cd, likely due to the 4d series moderate polarizability and primogenic repulsion from inner core d-electrons [70,71]. This indicates that the value of $V_{\text{max}}$ on M atom became more positive as the halogen was less polarizable. The $V_{\text{min}}$ of $sp^2$-hybridized ethylene was slightly more negative than that in acetylene. For the acetylene system, electron-withdrawing atom F increased the $V_{\text{min}}$, and electron-donor atom Li became $V_{\text{min}}$ more negative.

![Figure 1. MEP surfaces of ZnBr$_2$ and $\pi$ systems at the MP2/aug-cc-pVTZ(PP) level of theory at the 0.001 electrons Bohr$^{-3}$. Cyan and yellow balls on the surface correspond to $V_{\text{min}}$ and $V_{\text{max}}$, respectively. All are in kcal/mol.](image)
This indicates that there is a stronger charge transfer in the π to the charge transfer between the highest π-occupied orbitals of the unsaturated moiety and the lowest unoccupied orbitals of the MX₂ moiety. The α in P form is smaller than that in the T form. For example, the α is 149° in ZnBr₂····C₂H₂·P and 158° in ZnBr₂····C₂H₂·T. This indicates that there is a stronger charge transfer in P form than that in the T form. What is more, the curvature increases with the order Hg, Cd, and Zn, and the bending diminishes with the decrease of halogen atomic number.
Table 2. Binding distance (R_{M···*} in Å) between the M in MX₂ and the centers of C–C bond in π molecules (* denotes the center of C–C bond), M–X (R_{M-X} in Å) and C–C bond length (R_{C-C} in Å) of complexes, X-M-X angle (α in degrees), and dihedral angle of X-X···C–C (θ in degrees), and interaction energies (ΔE, kcal/mol) in the complexes.

| Complexes          | R_{M···*} | R_{M-X} | R_{C-C} | α  | θ   | ΔE  |
|--------------------|-----------|---------|---------|----|-----|-----|
| ZnBr₂···C₂H₂–P     | 2.387     | 2.222   | 1.219   | 149| 0   | −9.72 |
| CdBr₂···C₂H₂–P     | 2.670     | 2.401   | 1.218   | 161| 0   | −8.26 |
| HgBr₂···C₂H₂–P     | 3.078     | 2.363   | 1.215   | 175| 0   | −2.96 |
| ZnBr₂···C₂H₂–T     | 2.538     | 2.204   | 1.216   | 158| 83  | −5.29 |
| CdBr₂···C₂H₂–T     | 2.770     | 2.389   | 1.216   | 165| 83  | −5.24 |
| HgBr₂···C₂H₂–T     | 3.083     | 2.359   | 1.214   | 176| 84  | −1.78 |
| ZnBr₂···C₂H₄–P     | 2.367     | 2.225   | 1.347   | 146| 0   | −10.89 |
| CdBr₂···C₂H₄–P     | 2.635     | 2.406   | 1.344   | 157| 0   | −8.58 |
| HgBr₂···C₂H₄–P     | 3.051     | 2.364   | 1.338   | 174| 0   | −2.12 |
| ZnBr₂···C₂H₄–T     | 2.400     | 2.216   | 1.346   | 153| 82  | −9.51 |
| CdBr₂···C₂H₄–T     | 2.640     | 2.401   | 1.344   | 163| 82  | −8.17 |
| HgBr₂···C₂H₄–T     | 2.924     | 2.365   | 1.339   | 175| 82  | −2.30 |
| ZnBr₂···C₂F₂–P     | 2.886     | 2.184   | 1.199   | 171| 42  | −1.26 |
| CdBr₂···C₂F₂–P     | 2.976     | 2.276   | 1.199   | 174| 40  | −2.39 |
| HgBr₂···C₂F₂–P     | 3.152     | 2.355   | 1.197   | 179| 46  | −1.03 |
| ZnBr₂···C₂Li₁–P    | 1.968     | 2.348   | 1.276   | 119| 0   | −99.94 |
| CdBr₂···C₂Li₁–P    | 2.172     | 2.534   | 1.279   | 132| 0   | −89.97 |
| HgBr₂···C₂Li₁–P    | 2.152     | 2.543   | 1.289   | 126| 0   | −87.51 |

The binding distance R_{M···*} defined as the distance between the M atom of MX₂ and the center of C–C bond in C₂H₂ or C₂H₄ is in the wide range of 2.4–3.1 Å, which is longer than that in MCO₃ (M = Zn, Cd, Hg)···nitrogen-containing bases (HCN, NH₂CH₂, NH₃) (1.9–2.2 Å) [20] and ZnX₂···carbene (2.0–2.2 Å) [15] or (2.12–2.20 Å) [16]. It shows that there is a spodium–π bond between MX₂ and C₂H₂ or C₂H₄. In general, the R_{M···*} becomes shorter in the order of Hg→Cd→Zn. For example, ZnX₂···C₂H₂–P (2.387–2.406 Å) is shorter by 0.3 Å than that in CdX₂···C₂H₂–P (2.664–2.700 Å) and 0.7 Å in HgX₂···C₂H₂–P (3.056–3.145 Å). In addition, with the increase of the halogen atomic number, the R_{M···*} increases by 0.04 Å in CdX₂···C₂H₂–P and 0.09 Å in HgX₂···C₂H₂–P, although it decreases by 0.02 Å in ZnX₂···C₂H₂–P. Compared with MX₂···C₂H₂–P dimers, the R_{M···*} of MX₂···C₂H₂–T has an elongation (0.02–0.19 Å) except ZnBr₂···C₂H₂–T and ZnBr₂···C₂H₂–T. The M···* distance of MX₂···C₂H₂–P shortens by 0.01–0.05 Å than that in MX₂···C₂H₂–P. Compared to MX₂···C₂H₂–P, the change of R_{M···*} in MX₂···C₂H₄–T is about −0.1 Å.

The interaction energies ΔE between MX₂ and C₂H₂ or C₂H₄ are larger in the order of Hg < Cd < Zn (from −1.37 kcal/mol to −11.68 kcal/mol at the MP2/aug-cc-pVTZ level), although weaker than the interaction energy of MCO₃ (M = Zn, Cd, Hg)···nitrogen-containing bases (HCN, NH₂CH₂, NH₃) complex (−31 kcal/mol to −56 kcal/mol at the MP2/aug-cc-pVTZ level) [20], and dissociation energy of ZnX₂···carbene (10–79 kcal/mol at the ωB97X-D/6-311++G(2df,2p) level) [15] or (18.5–27.4 kcal/mol at the MN15/6-311+G(d) level) [16]. The ΔE of the Zn-containing binary is 3–6 times that of the Hg-containing binary. The order of ΔE is inconsistent with the order of V_{max} value of the electrostatic potential of M (Hg < Zn < Cd). We predict that there are other types of interaction components besides the electrostatic one, which is dominant in the formation of the spodium bond [20]. The coexistence of strong attractive (blue regions), weak attractive (green regions), and strong repulsion (red regions) interactions (Figures S2–S5, in Section 3.5) seems to prove this. In addition, the interaction energies are stronger in the order of I < Br < Cl. This trend of interaction energies could be demonstrated by the electrostatic interactions between the positive MEPs of Zn/Cd/Hg and the negative ones of C₂H₂ or C₂H₄. The interaction energy analysis shows that both hybridizations have a small difference as well as. The V_{min} of C₂H₂ (−14.63 kcal/mol) and C₂H₄ (−14.78 kcal/mol)
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is similar, which explains the aforementioned phenomenon. It indicates that the carbon hybridization of the Lewis base has a faint effect on the spodium–π bond.

3.3. Substituent Effect

To explore the substitution effect on the spodium–π bond, we replaced the H atom in MX₂····C₂F₂–P with F or Li. The interactions in the F-substituted complexes MX₂····C₂F₂–P became weaker than that in MX₂····C₂H₂–P, characterized by a longer binding distance \( R_{M···}\) (~0.5 Å in ZnX₂····C₂F₂–P, ~0.3 Å in CdX₂····C₂F₂–P, less than 0.1 Å in HgX₂····C₂F₂–P) and smaller interaction energy (~0.79 kcal/mol to ~3.25 kcal/mol: in the order of Hg < Zn < Cd). This was due to the large electron-withdrawing ability of F, which significantly decreased the negative MEPs of C₂F₂. As a consequence, the interaction energies between MX₂ and C₂F₂ became weaker, with a long binding distance. The order of interaction energy was consistent with the order of \( V_{\text{max}} \) value on M (Hg < Zn < Cd), and the decreased magnitude of interaction energy in MX₂····C₂F₂–P was in the order of Zn (~8 kcal/mol) < Cd (~6 kcal/mol) < Hg (~1 kcal/mol). This confirms the important role of electrostatic interactions in MX₂····C₂F₂–P system. In addition, the \( \alpha \) close to 180°, and the dihedral angle \( \theta \) increased from 0° to 33–52°. It indicates that the repulsion interactions decreased. This is illustrated by the original red regions turning orange in Figure S6.

On the contrary, the interaction for MX₂····C₂Li₂–P was strengthened with a shorter binding distance and larger interaction energy (approximately 9–20 times). The change of binding distance \( R_{M···}\) in MX₂····C₂Li₂–P was obvious, shortened by 0.4 Å in ZnX₂····C₂Li₂–P, 0.5 Å in CdX₂····C₂Li₂–P, 0.9 Å in HgX₂····C₂Li₂–P. The shorter binding distance was ascribed to the increase of electrostatic interaction between MX₂ and C₂Li₂, resulting in the more negative MEPs of C₂Li₂. Compared with MX₂····C₂H₂–P, although the increased multiple of interaction energy was ~9 times for ZnX₂····C₂Li₂–P, ~10 times for CdX₂····C₂Li₂–P, and ~25 times for HgX₂····C₂Li₂–P, the interaction energies for MX₂····C₂Li₂–P were stronger in the order of Hg < Cd < Zn. What is more, the molecular deformation for MX₂····C₂Li₂–P (\( \alpha \): 117–134°) was more significant than that in MX₂····C₂H₂–P, which can be chalked up to strong interaction energies. It shows that other forms of interaction components (Figure S7) beyond electrostatic effects also play an important role.

The charge transfer CT in the complexes is presented in Table S2. The negative charge transfer confirms the Lewis acid roles for the MX₂····C₂Li₂–P system. In addition, the MEPs of C₂Li₂ (~0.020 e) were stronger than that in MX₂····C₂H₂–P (~0.043 e) due to their electron-withdrawing nature, whereas the electron donor Li increases the charge transfer (~0.070 e to ~1.293 e).

The second-order perturbation energies \( (E^{(2)}) \) of spodium–π interaction is analyzed with mainly orbital interaction BD\(_{C≡C→LP^*M}\), where BD\(_{C≡C}\) denotes the C=C bonding orbital, and LP\(^*\)\(_M\) is the lone pair anti-bonding orbital of the Group 12 atom. Accompanied with these orbital interactions, there occurs a charge transfer from ethyne/ethene to MX₂, confirmed by the negative charge on MX₂ [15,24]. The Group 12 elements are usually considered to be post-transition or main group elements and are not labeled as transition metals [72]. Using the traditional DCD model [73] cannot interpret well the spodium–π interaction. It is necessary to point out that there are other orbital interactions in the spodium–π interaction. The orbital interactions in HgX₂····C₂H₂–P are much weaker than those in CdX₂····C₂H₂–P and ZnX₂····C₂H₂–P, indicating the partial covalent characteristics of the latter two systems. For the same metal in MX₂, \( E^{(2)} (BD_{C≡C→LP^*M}) \) becomes higher with the increase of X atomic number, which is in the reverse order of the corresponding systems’ interaction energy. We attribute this inconsistency to the coexistence of spodium bond, the X···H interactions, and coulomb repulsive interaction.

3.4. AIM

The existence of spodium–π interaction is further characterized with the presence of BCPs between the M atoms and π system (Figure S8). Electron density (\( \rho \)), Laplacian (\( \nabla^2 \rho \)),

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and total energy density ($H$) at the intermolecular BCPs of the complexes are listed in Table 3
and Table S3. The $\rho$ value for the spodium–π interaction containing Zn and Cd is about
0.03–0.04 au, which is smaller than that in MCO$_3$ (M = Zn, Cd, Hg) · · · nitrogen-containing
bases (HCN, NHCH$_2$, NH$_3$) complex (0.08 au) [20], and of ZnX$_2$ (X = H, Me, Et or F, Cl, Br) with carbenes or carbodiphosphoranes (0.07–0.11 au) [15,16]. For most complexes,
the electron density is larger with the increase of the interaction energy. However, this
law is not applicable to the Zn containing systems, mainly because of the existence of
strong repulsion resulting from the orbital interaction between the Zn–X bonding and C–H
bonding of C$_2$H$_2$/C$_2$H$_4$. Hence, the strength of spodium–π bond in most cases can be
measured by the topological parameters, particularly the electron density. F substituents
prominently decrease the electron density of Zn and Cd systems due to their electron-
withdrawing nature, whereas the electron density changes slightly for the system containing
Hg. Compared with MX$_2$ · · · C$_2$H$_2$–P, the stronger electron donor Li increases the electron
density by approximately 2–6 times, reached up to 0.07–0.08 au. The values of $\rho$ increase in
the order of Hg < Cd < Zn, which is the same as the order of interaction energies.

| Complexes          | $\rho$    | $\nabla^2 \rho$ | $H$    |
|--------------------|-----------|----------------|--------|
| ZnBr$_2$ · · · C$_2$H$_2$–P | 0.0398 | 0.1023         | −0.0076|
| CdBr$_2$ · · · C$_2$H$_2$–P | 0.0292 | 0.0863         | −0.0018|
| HgBr$_2$ · · · C$_2$H$_2$–P | 0.0160 | 0.0480         | 0.0009 |
| ZnBr$_2$ · · · C$_2$H$_2$–T | 0.0297 | 0.0754         | −0.0037|
| CdBr$_2$ · · · C$_2$H$_2$–T | 0.0242 | 0.0708         | −0.0006|
| HgBr$_2$ · · · C$_2$H$_2$–T | 0.0157 | 0.0468         | 0.0009 |
| ZnBr$_2$ · · · C$_2$H$_4$–P | 0.0421 | 0.0893         | −0.0091|
| CdBr$_2$ · · · C$_2$H$_4$–P | 0.0319 | 0.0817         | −0.0030|
| HgBr$_2$ · · · C$_2$H$_4$–P | 0.0175 | 0.0463         | 0.0005 |
| ZnBr$_2$ · · · C$_2$H$_4$–T | 0.0393 | 0.0843         | −0.0078|
| CdBr$_2$ · · · C$_2$H$_4$–T | 0.0315 | 0.0807         | −0.0028|
| HgBr$_2$ · · · C$_2$H$_4$–T | 0.0220 | 0.0570         | −0.0003|
| ZnBr$_2$ · · · C$_2$F$_2$–P | 0.0158 | 0.0412         | 0.0001 |
| CdBr$_2$ · · · C$_2$F$_2$–P | 0.0168 | 0.0486         | 0.0005 |
| HgBr$_2$ · · · C$_2$F$_2$–P | 0.0140 | 0.0423         | 0.0010 |
| ZnBr$_2$ · · · C$_2$Li$_2$–P | 0.0878 | 0.2251         | 0.0069 |
| CdBr$_2$ · · · C$_2$Li$_2$–P | 0.0738 | 0.2095         | −0.0189|
| HgBr$_2$ · · · C$_2$Li$_2$–P | 0.0869 | 0.2212         | −0.0255|

It has been confirmed that the type of interactions can be classified in the light of the
sign of $\nabla^2 \rho$ and $H$ [74]. Positive $\nabla^2 \rho$ and $H$ indicate a purely closed-shell interaction. The
partially covalent nature can be confirmed by the positive $\nabla^2 \rho$ and negative $H$ [75,76].
For the spodium–π interaction of HgX$_2$ · · · C$_2$H$_2$–P, HgX$_2$ · · · C$_2$H$_2$–T, and HgX$_2$ · · · C$_2$F$_2$–P,
HgX$_2$ · · · C$_2$H$_4$–P in which Hg is the Lewis acid, both $\nabla^2 \rho$ and $H$ are positive, corresponding
to a purely closed-shell interaction. However, the $\nabla^2 \rho$ is positive and the $H$ is negative for
the complexes containing Zn and Cd, indicating a partially covalent interaction [74,77,78].
The SpB involving lone pairs [20], anions [18], carbenes, or carbodiphosphoranes [15] are
also characterized by a degree of covalence. Thus, in combination with the high interaction
energies as discussed above, spodium–π interaction containing Zn and Cd has a partially
covalent nature. Both $\nabla^2 \rho$ and $H$ are positive in MX$_2$ · · · C$_2$F$_2$–P, corresponding to a purely
closed-shell interaction. Positive $\nabla^2 \rho$ and negative $H$ confirm the partially covalent nature
interaction for MX$_2$ · · · C$_2$Li$_2$–P. This shows that the substituent atoms of π system change
the nature of spodium–π interaction.

It is interesting to check the quality of the exponential relationship between the interaction
energy $\Delta E$ and the binding distance $R_M$ · · · *, or the charge transfer CT, or the electron density
$\rho$ at the BCP. Three of all (Figure 3a–c) display an exponential relationship with the $\Delta E$, with a
correlation coefficient of ~0.99. Thus, they can be used to estimate the change of spodium–π interaction strength. In addition, there is an exponential relationship between CT and ρ (Figure 3d). A greater value of ρ means more charge transfer between MX₂ and π systems.

3.5. NCI Analyses

Noncovalent interaction analysis (NCI) provides the graphical visualization of the regions where non-covalent interactions occur in real-space, which was capable of distinguishing van der Waals interactions and repulsive steric interactions [79,80]. NCI analysis also offers continuous surfaces through color codes, which is able to recognize the attractive or repulsive nature of the interactions and to decide their relative strength on a qualitative but visual basis. To our knowledge, this technique was carried out for the spodium bond [4,15,16,20]. Thus, we are interested in the deep insights that NCI method can provide for the complexes between MX₂ and π systems. NCI analysis for some complexes is depicted in Figure 4, and the analysis for all complexes is shown in Figures S2–S7. The color-mapped isosurfaces and corresponding scatter diagrams of RDG versus sign(λ₂)ρ for the investigated complexes are also given.
In MX$_2$⋯C$_2$H$_2$–P (Figure S2), there are two spikes in the negative value of the abscissa. The more negative one (about −0.04 a.u. for Zn in Figure S2a–c, −0.03 a.u. for Cd in Figure S2d–f, −0.02 a.u. for Hg in Figure S2g–i) represents the spodium–π interaction, characterized by a large blue or green disc. The less negative spike (−0.01 a.u.) is referred to the two regions of weak X⋯H interaction between the H of C$_2$H$_2$ and X of MX$_2$, shown by flakes. Evidently, the weak X⋯H interaction cannot be detected in the AIM but can with the NCI method. The former interaction is evidently stronger than that of the latter. Between the two interactions mentioned above, a red or orange region indicates a repulsive interaction, which accounts for the coulomb repulsive interaction. In MX$_2$⋯C$_2$H$_2$–T (Figure S3), there is only one spike in the negative value of the abscissa representing spodium–π interaction. Moreover, the spike in MX$_2$⋯C$_2$H$_2$–T is less negative than that in the P form. It indicates that the spodium–π interaction in the P form is stronger than that in the T form. For MX$_2$⋯C$_2$H$_4$–P (Figure S4), the spodium–π spike (−0.02 a.u. to −0.04 a.u.) and repulsive spike are analogous to MX$_2$⋯C$_2$H$_2$–P. The spike of X⋯H interactions disappears in ZnX$_2$⋯C$_2$H$_4$–P (Figure S4a–c) and CdX$_2$⋯C$_2$H$_4$–P (Figure S4d–e) and appears in HgX$_2$⋯C$_2$H$_4$–P (Figure
S4f–g). For MX\textsubscript{2}⋯C\textsubscript{2}H\textsubscript{4}–T (Figure S5), the spodium–\textpi spike and repulsive spike in a narrow region is present, and the X⋯H interactions’ spike is disappeared.

For F-substituted systems, there are similarities with MX\textsubscript{2}⋯C\textsubscript{2}H\textsubscript{2}–P. The MX\textsubscript{2}⋯C\textsubscript{2}F\textsubscript{2}–P complexes (Figure S6) have two attractive and one repulsive spikes. The spike representing the spodium–\textpi interactions moves to the right direction of the X-axis than that in MX\textsubscript{2}⋯C\textsubscript{2}H\textsubscript{2}–P, indicating the weakening of spodium–\textpi interaction. The X⋯F interactions are also shown (less −0.01 a.u.), which is weaker than the X⋯H interactions in MX\textsubscript{2}⋯C\textsubscript{2}H\textsubscript{2}–P. For the Li system (Figure S7), the spodium–\textpi interaction spike moves to the more negative of the X-axis (−0.06 a.u. to −0.08 a.u.) than MX\textsubscript{2}⋯C\textsubscript{2}H\textsubscript{2}–P, indicating the enhancement of the spodium–\textpi interaction. The X⋯Li interaction spikes are on the −0.02 a.u. Two additional blue discs around −0.04 a.u. between Li and C in C\textsubscript{2}Li\textsubscript{2} indicate attractive interactions.

3.6. Electron Density Shift

Figure 5 illustrates the maps of electron density shifts in the ZnBr\textsubscript{2}⋯π systems, which are generated by the difference between the density of the optimized complex and the sum of individual monomers in their same internal geometries. The electron density shifts of all complexes are shown in Figures S9–S14. The increases in density arising from the interaction are illustrated in the red regions and losses shown in the blue areas. The most prominent feature is a red region in the interaction space M⋯π and a blue region of density depletion on the M atom. This feature indicates the presence of spodium–\textpi interaction. It is found that there is a buildup of the electron density on the halogen atoms in MX\textsubscript{2} and electron loss occurs on the H/F/Li atoms in π systems. This confirms the X⋯H/F/Li interaction. Besides, density depletion is observed on the M–X of MX\textsubscript{2}. Considering the electron loss on the H/Li atoms in π systems, it provides evidence for the steric interactions between the H/Li atoms and the M–X.

![Figure 5](image-url)

**Figure 5.** Electron density shifts of selected binary complexes (iso = ± 0.0008). Red regions indicate increased electron density, while blue regions represent decreased electron density.

3.7. Energy Decomposition

A decomposition of interaction energy provides valuable insight into understanding the physical pictures of all binary complexes. The physical components from GAMESS,
including electrostatic (ES), exchange (EX), repulsion (REP), polarization (POL), and dispersion (DISP) energies for some representative complexes, are presented in Table 4. More details are seen in Table S4 and Figure S15. Between MX2 and C2H2/C2H4, the remarkable overlap of molecular orbitals results in a large EX and a much larger REP. The exchange energy is chiefly caused by the overlap of molecular orbitals, and it is more negative in the P form than in the T form. Considering both EX and REP are mutually dependent, the following discussion is not focused on them. For most complexes (Figure S15a–d), the magnitude of ES is more negative than POL and DISP, indicating that the electrostatic interaction is dominant to the total interaction energy of the spodium–π bonding. For Zn/Cd containing complexes, three attractive terms (ES, POL, and DISP) become more negative in the order of DISP < POL < ES, and ES is about twice as much as POL. However, for the Hg complexes, the order is POL < DISP < ES, and POL is nearly equal to DISP. It indicates that the contribution of POL and DISP cannot be ignored. On the other hand, with the variation of halogen substituent for a given Group 12 metal, a little energy difference is found in the energy components, that is, halogen substituents have little effect on the nature of the spodium–π interaction.

Table 4. Electrostatic energy (ES), exchange energy (EX), repulsion energy (REP), polarization energy (POL), and dispersion energy (DISP) in the selected complexes. All are in kcal/mol.

| Complexes              | ES   | EX   | REP  | POL  | DISP  |
|------------------------|------|------|------|------|-------|
| ZnBr2⋯C2H2⋯P           | −31.95 | −51.86 | 96.03 | −18.31 | −5.66 |
| CdBr2⋯C2H2⋯P           | −23.41 | −38.14 | 69.28 | −11.88 | −5.65 |
| HgBr2⋯C2H2⋯P           | −10.75 | −20.25 | 35.06 | −3.99  | −4.70 |
| ZnBr2⋯C2H2⋯T           | −18.09 | −34.58 | 62.46 | −11.21 | −5.46 |
| CdBr2⋯C2H2⋯T           | −14.02 | −27.28 | 48.73 | −8.27  | −5.60 |
| HgBr2⋯C2H2⋯T           | −7.14  | −17.03 | 29.18 | −3.34  | −5.11 |
| ZnBr2⋯C2F2⋯P           | −7.24  | −18.32 | 32.41 | −4.09  | −5.88 |
| CdBr2⋯C2F2⋯P           | −6.89  | −17.67 | 31.40 | −4.21  | −6.34 |
| HgBr2⋯C2F2⋯P           | −4.47  | −13.30 | 23.02 | −2.17  | −6.04 |
| ZnBr2⋯C2Li2⋯P          | −171.59 | −175.81 | 340.82 | −86.87 | −10.41 |
| CdBr2⋯C2Li2⋯P          | −157.82 | −166.35 | 322.57 | −81.82 | −11.45 |
| HgBr2⋯C2Li2⋯P          | −169.45 | −211.53 | 410.98 | −118.60 | −10.72 |
| ZnBr2⋯C2H4⋯P           | −33.38 | −57.61 | 106.78 | −20.80 | −7.76 |
| CdBr2⋯C2H4⋯P           | −24.55 | −43.50 | 79.30 | −14.31 | −7.45 |
| HgBr2⋯C2H4⋯P           | −11.32 | −24.16 | 41.93 | −4.88  | −6.11 |
| ZnBr2⋯C2H4⋯T           | −29.13 | −49.86 | 92.49 | −17.69 | −7.18 |
| CdBr2⋯C2H4⋯T           | −22.86 | −40.02 | 73.28 | −13.14 | −7.27 |
| HgBr2⋯C2H4⋯T           | −13.64 | −28.38 | 50.07 | −6.44  | −6.75 |

The strong electron-withdrawing group F (Figure S15e) causes a great reduction of ES and POL, especially in ZnX2⋯C2F2⋯P and CdX2⋯C2F2⋯P. In both systems, ES is the most negative, followed by DISP, and POL is the least negative. The ES contribution is comparable with that of DISP. However, in HgX2⋯C2F2⋯P, the order is DISP > ES > POL, which is inconsistent with that in HgX2⋯C2H2⋯P, indicating that the DISP contribution is dominant. Interestingly, Li group results in a sharp increase of ES and POL and has a slight effect on DISP. Moreover, the MX2⋯C2Li2⋯P complexes are dominated by electrostatic energy. The relatively large POL (−80.70 kcal/mol to −119.31 kcal/mol) suggests that the orbitals undergo a significant change in their shapes, a typical character in the formation of covalent bonds, conforming the partially covalent nature of spodium–π interaction in MX2⋯C2Li2⋯P (Figure S15f). Obviously, the substituent of Lewis acid has a prominent effect on the nature of spodium–π interaction.

3.8. Comparison

There are a number of reports about the interactions including π systems, such as π–hydrogen bond [26–30], π–lithium bond [31–33], π–beryllium bond [34], π–triels bond [41],
In addition, we compare the geometric energetic of SpB formed by molecules containing Group 12 atoms and varied molecules, such as lone-pair-containing molecules [1,11,12,14,20], anions [18], carbones, and carbodiphosphoranes [15], and π systems. Some typical SpB’s examples are listed in Table 6. In these complexes of SpB, the binding distance R is in a range of 1.879–3.616 Å and the interaction energy ranges from −0.79 kcal/mol to −106.75 kcal/mol. The longest distance presents in the anionic dimer (HgCl_3^-) in water medium (3.62 Å), and the interaction energy is only −1.88 kcal/mol [18]. This anionic crystal structure attributes to the noncovalent spodium bonds and crystal packing forces. The interaction energy provides a wide range from −2.2 kcal/mol to −56.68 kcal/mol for the SpB involving lone pair electrons [1,20], which is dominated by electrostatics or polarization [20]. The π systems as a Lewis base participate in the formation of SpB, which

| Complexes | R (Å) | ΔE (kcal/mol) | Method | Types         | Reference |
|-----------|-------|---------------|--------|---------------|-----------|
| F–C–H     | 0.931 | −2.88         | MP2/aug-cc-pVTZ | π-hydrogen   | [30]      |
| F–C–H     | 0.932 | −2.87         | ΔE_{bind(BSSE)} | π-lithium    | [33]      |
| FLi–C–H   | 2.356 | −7.73         | MP2/6-311+G(d,p) | π-sodium     | [35]      |
| FLi–C–H   | 2.352 | −7.72         | ΔE_{bind(BSSE)} | π-sodium     | [35]      |
| FNa–C–H   | 2.760 | −5.20         | MP2/6-311+G(d,p) | π-sodium     | [35]      |
| FNa–C–H   | 2.808 | −5.23         | ΔE_{bind(BSSE)} | π-sodium     | [35]      |

Table 5. Binding distance (R in Å) and interaction energy (ΔE in kcal/mol) for some interactions, including π systems.
further complements the concept of spodium bond. The adjustment of the SpB’s strength in a wider range (−0.79 kcal/mol to −106.75 kcal/mol) is realized.

Table 6. Binding distance (\(R\) in Å) and interaction energy (\(\Delta E\) in kcal/mol) for some typical examples of spodium bonds.

| Lewis Acid  | Lewis Base       | \(R\)  | \(\Delta E\) | Reference |
|------------|------------------|--------|--------------|-----------|
| ZnBr₂L₂ (L = thiourea) | CO     | 3.79   | −2.2 \(\dagger\) | [1]       |
| CdCl₂L₂ (L = thiourea) | H₂CS   | 2.95   | −8.9 \(\dagger\) |           |
| CdCO₃      | NCH    | 2.146  | −31.84 \(\dagger\) |           |
| HgCO₃      | NHCH₂  | 2.047  | −56.68 \(\dagger\) |           |
| HgCl₃\(^{-}\) | HgCl₃\(^{-}\) | 3.616  | −1.88 \(\dagger\) |           |
| ZnMe₂      | cyclopropenyldiene | 2.192  | 10.3 \(\dagger\) |           |
| ZnF₂       | (NH₃)₂C | 1.879  | 78.8 \(\dagger\) |           |
| HgI₂       | C₂F₂   | 3.177  | −0.79 |           |
| ZnCl₂      | C₂Li₂  | 1.965  | −106.75 | Our results |

\(\dagger\): RI-MP2/aug-cc-pVTZ-based interaction energies. \(\dagger\): MP2/aug-cc-pVTZ-based BSSE-corrected interaction energies.

4. Conclusions

The MX₂ as the Lewis acid engages in spodium–\(\pi\) bonds with \(\pi\) systems, and two different binding types (\(P\) or \(T\) form) are obtained. These complexes between the MX₂ (\(M = \text{Zn, Cd, and Hg}; X = \text{Cl, Br and I}\)) and \(\pi\) system were investigated in view of the equilibrium structure, energetics, electrostatic potential, AIM, NCI, and energy decomposition. The total interaction consists of several parts: spodium–\(\pi\) interaction, X···H/F/Li weak interaction and repulsion interaction. Spodium–\(\pi\) interaction is the principal, while the other two should not be ignored. Generally, the spodium–\(\pi\) interaction becomes stronger in the order Hg < Cd < Zn. The enhancing effect of the halogen substituent on the MX₂ is more prominent in the order of I < Br < Cl. With the increase of electronegativity of the substituents on the Lewis acid, the interaction energies increase. For the Lewis base, the interaction energies decrease with increasing electronegativity of the substituents. The nature of interactions is related to the Group 12 metals and \(\pi\) systems. The spodium–\(\pi\) interaction of complexes containing C₂H₂ or C₂H₄ is dominated by electrostatic energy, especially for Zn and Cd with a partially covalent contribution, while a purely closed-shell nature for Hg. In the complexes containing C₂F₂, dispersion is comparable with that of electrostatic. Even in HgX₂···C₂F₂–\(P\), dispersion contribution exceeds that of electrostatic energy. It is worth mentioning that no one plays the sole role. Our results further extend the concept of spodium bond and provide support for the adjustment of the spodium bonds’ strength in a wider range.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27092885/s1, Table S1: distances (\(R, \text{Å}\)) between M in MX₂ and the centers of C–C bond in \(\pi\) molecules (* denote the centers of C–C bond), angles of X-M-X in MX₂ (\(\alpha, \text{deg}\)), dihedral angle of X-X···C–C (\(\beta, \text{deg}\)), and interaction energy (\(\Delta E, \text{kcal/mol}\)) in the complexes at the MP2/aug-cc-pVTZ level. Table S2: charge transfer (CT, e), second-order perturbation energies (\(E^{(2)}\), kcal/mol) and Wiberg bond index (WBI) in the complexes at the HF/aug-cc-pVTZ level. Table S3: electron density (\(\rho, \text{au}\)), Laplacian (\(\nabla^{2}\rho, \text{au}\)), and total energy density (\(H, \text{au}\)) at the intermolecular bond critical points (BCPs) in the complexes at the MP2/aug-cc-pVTZ level. Table S4: electrostatic energy (ES), exchange energy (EX), repulsion energy (REP), polarization energy (POL), and dispersion energy (DISP) in the selected complexes at the MP2/aug-cc-pVTZ level. All are in kcal/mol. Figure S1: the optimized geometries of the MX₂ (\(M = \text{Zn, Cd, Hg}; X = \text{Cl, Br, I}\)) and the corresponding NCI maps of the corresponding binary complexes. Blue, green, orange, and red areas correspond to strong attractive, weak attractive, weak repulsive, and strong repulsive interactions, respectively. The energies (\(\Delta E\)) in kcal/mol are indicated in the top right corner of each panel. Figure S2: plots of the reduced density gradient RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(\(\lambda_2\))) of MX₂···C₂F₂–\(P\). NCI maps of the corresponding binary complexes. Blue, green, orange, and red areas correspond to strong attractive, weak attractive, and weak repulsive interactions, respectively.
weak repulsive, and strong repulsive interactions, respectively. Figure S3: plots of the reduced density gradient RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ2)) of MX2···C2H2···T. NCI maps of the corresponding binary complexes. Figure S4: plots of the reduced density gradient RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ2)) of MX2···C2H4···P. NCI maps of the corresponding binary complexes. Figure S5: plots of the reduced density gradient RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ2)) of MX2···C2H4···T. NCI maps of the corresponding binary complexes. Figure S6: plots of the reduced density gradient RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ2)) of MX2···C2Li2···T. NCI maps of the corresponding binary complexes. Figure S7: plots of the reduced density gradient RDG versus the electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ2)) of MX2···C2F2···T. NCI maps of the corresponding binary complexes. Figure S8: molecular graphs of spodium–π bonded stable complexes at the intermolecular bond critical points. Figure S9: electron density shifts of the MX2···C2H2···T complexes (iso = ±0.0008). Red regions indicate increased electron density, while blue regions represent decreased electron density. Figure S10: electron density shifts of the MX2···C2H2···T complexes. Figure S11: electron density shifts of the MX2···C2H2···P complexes. Figure S12: Electron density shifts of the MX2···C2H2···T complexes. Figure S13: electron density shifts of the MX2···C2F2···P complexes. Figure S14: electron density shifts of the MX2···C2Li2···P complexes. Figure S15: comparison of electrostatic, polarization, and dispersion energies in the binary complexes.

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