Computational Study on Metal-Ion-Decorated Prismane Molecules for Selective Adsorption of CO₂ from Flue Gas Mixtures

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ABSTRACT: Selective adsorption of CO₂ from flue gas is extremely significant because of its increasing concentration in air and its deleterious effect on the environment. In this work, we have explored metal-ion-bound prismane molecules for selective CO₂ adsorption from the flue gas mixture. The Ca²⁺-bound prismane complex exhibits superior CO₂ selectivity and adsorption capacity. The calculated binding energy and molecular electrostatic potential (MESP) analysis showed that the rectangular face of prismane binds strongly with metal ions as compared to its triangular face. The CBS-QB3 and density functional theory-based functional M06-2X/6-311+G(d) calculations show that the prismane molecule can bind to one Li⁺, K⁺, Mg²⁺, and Ca²⁺ ion with favorable binding energy. The metal-ion-bound prismane complexes have been examined for their CO₂, N₂, and CH₄ adsorption capacity. Prismane−Ca²⁺ can bind with six CO₂ molecules strongly with an average binding energy of −18.1 kcal/mol as compared to six N₂ (−12.6) and five CH₄ (−13.4) gas molecules. The gravimetric density calculated for the CO₂-adsorbed prismane−Ca²⁺ complex has been found to be 69.1 wt %. The discrete hydrocarbon structure for selective separation of CO₂ is rare in the literature and can have potential applications for cost-effective CO₂ capture from the flue gas mixture.

INTRODUCTION

The world energy demand is of concern with the increasing population and continuous economic growth.¹ To meet such demands, fossil fuels will be the dominating source of energy globally. Therefore, the effective means of CO₂ capture and storage is warranted. Reduction of CO₂ level is important from a socio-economic view and captured CO₂ can further act as a renewable feedstock if it is converted to formic acid, CO, or hydrocarbon products.² Post-combustion CO₂ capture is found to be the most feasible route for separation of CO₂ from the flue gas effluent of power plants as such adsorption takes place at atmospheric pressure and a lower concentration of CO₂.³ In recent years, solid materials have been newly developed as an alternative to amine scrubbing for low-cost CO₂ capture from flue gas. A large range of porous materials have been developed among such materials, that is, the metal–organic frameworks (MOFs) with unsaturated metal centers are well known for their high adsorption capacities.⁴ The presence of strong and selective adsorption sites allows it to adsorb even from low-concentration streams. However, such materials have a less recyclable property and even less structural integrity.⁵ Therefore, storage materials must have a balance of structural stability as well as adsorption capacity. Several efforts have been made to develop such materials, and still, the efforts are going on in this direction to design materials with requisite properties. One of the approaches to achieve thermal stability is the use of modified carbon-based materials. Materials such as nitrogen-doped carbons and potassium-tethered carbons do have better CO₂ adsorption capacity than pure carbons with better adsorption enthalpies.⁶ However, these materials also suffer demerit-like decomposition with increasing temperature, and these can further be improved for thermal stability and adsorption capacity as well. All the recent carbon-based materials reported for CO₂ adsorption are mainly the porous structures⁷,⁸ or modified graphene surfaces,⁹,¹⁰ and no molecular system is reported for CO₂ adsorption. The limitations of carbon-based porous materials are large complexity in pore textures, particularly surface heterogeneity due to which it is difficult to precisely calculate the contribution of each parameter, and the delicate control on pore size, especially for CO₂ separation.⁵,¹¹ Therefore, there is a need to understand different carbon structure materials and to tailor them for improving the CO₂ separation. There are several reports where metal-decorated molecular systems such as cubane, cyclohexane, benzene, and adamantane are used for the hydrogen…
adsorption process. However, such discrete carbon materials have not been exploited for CO₂ separation from flue gas mixture.

Prismane is a polycyclic hydrocarbon and one of the interesting chemical compounds because of its unusual bonding features and symmetrical structure. The six carbon atoms are arranged in such a fashion that the two triangular faces are joined by three rectangular rings and form a highly strained framework. The bond angles significantly deviate from the tetrahedral angle of sp³-hybridized carbon, and the high degree of the π-character of the C−C−H bond due to the rehybridization of the carbon centers caused by steric strain shortened the C−C−H bonds. The synthesis procedure for prismane is reported, and it is found to be stable at room temperature. Prismane is known to be the valence isomer of benzene and stores more energy than benzene; however, the conversion of prismane to benzene is symmetry-forbidden, and this allows prismane to exist. The experimental data suggest that there is a bonding of C−C−C− bonds along the edges of triangular faces by 19° and on rectangular faces of prismane by 7.5°. The presence of magnetic fields perpendicular to either triangular or rectangular faces showed the unusual magnetic properties for prismane molecules. A very strong paratropic current flows around the C₂-axis and shields a large part of a rectangular face and extends in the vertical direction, and a delocalized diatropic ring current flows in the external regions on both faces. On the rectangular face, its modulus is 0.06 au, comparable with that of the benzene π-ring current of 0.08 au computed at the same level of theory. The presence of diatropic and paratropic currents on the triangular face of prismane has also been studied with the nucleus-independent chemical shift (NICS) analyses. The calculated electrostatic potentials on prismane describe the negative regions associated with the C−C−C− bonds, and the most negative regions are near the midpoints of the bonds. Therefore, these bonds can function as a preliminary site for the electrophilic attack. The presence of such bent C−C−C− bonds and electrostatic potentials is similar to the strained molecules such as cyclopropane. In this work, we have examined the metal-ion binding capacity of prismane and evaluated these metal-ion-bound complexes for adsorption of flue gas molecules such as carbon dioxide, nitrogen, and methane. We have examined lithium, potassium, magnesium, and calcium ions (Li⁺, K⁺, Mg²⁺, and Ca²⁺) binding to prismane as these ions are used widely for improving gas adsorption capacity. Prismane is found to be a liquid at room temperature. Recently, the liquid systems have also been important for gas adsorption with multiple merits such as easy continuous operation, easy loading and transporting gas guests in a flow system, and better adsorption capacity.

A number of derivatives of prismane such as polysiliconoprismanes, polynitroprismanes, polynitratriprismanes, and nitroestetrpirismane have been predicted as high-energy materials.

### RESULTS AND DISCUSSION

A variety of materials have been developed for flue gas separation such as zeolites, MOFs, polymers, and carbon-based materials such as activated carbon, graphene, and potassium-tethered carbons. Recently, metal-ion doping is used as a strategy for improving the gas adsorption capacity of materials. Many molecular systems have been examined for hydrogen adsorption such as metal-decorated benzene, cyclohexane, adamantane, cyclopropane systems, and B- and N-substituted carbon rings. Such molecular systems can be altered with appropriate modifications or decorated with metal ions for the use of flue gas separation. Prismane is known to be an interesting molecule with unusual bonding features such as cyclopropanes. The diatropic and paratropic ring currents on rectangular and triangular faces of prismane with bent bonds can bind with metal ions more efficiently. It is reported that the Li⁺ ion binds with antiaromatic systems, and lithium-ion resonance shifted to downfield because of the paramagnetic ring current. On the rectangular face of the prismane molecule, a very strong paratropic ring current flows, which therefore can be the probable site for metal-ion binding.

The literature report reveals that the potassium tethering with a carbon matrix can increase the CO₂ capturing capacity from the flue gas mixture. Calculating an interaction on the C₃N structure adsorbs CO₂ more uniformly than other transition metals such as Sc, Ti, V, Cr, Mn, Fe, and Co. Lithium-ion doping has been widely used to improve the CO₂ adsorption capacity of MOFs, phosphorene, lithium silicate, etc. We have exploited the Li⁺-, K⁺-, Mg²⁺-, and Ca²⁺-ion-decorated prismane molecules for the selective adsorption capability of flue gas molecules.

All geometries are optimized at the M06-2X/6-311+G(d) level of theory and the CBS-QB3 method for the interaction of metal ions with prismane and their interaction with flue gas molecules. The binding energies (ΔE) and Gibbs free energies (ΔG) of optimized prismane-metal-ion complexes at both methods show that the process of metal-ion binding is favorable at ambient temperature (Table 1). We have also evaluated the affinity of metal ions to the possible sites of the triangular and rectangular faces of the prismane molecule (Figure S1, Supporting Information). The binding energies of optimized geometries show that metal-ion binding to the rectangular face is energetically more favorable as compared to metal-ion binding to the triangular face and edges (Table S1). Geometries e and f converged to a similar binding mode to a (Table S1 and Figure S1). The optimized geometries of prismane with Li⁺, K⁺, Mg²⁺, and Ca²⁺ ions are shown in Figure 1. Table 1 shows that the Mg²⁺ has the highest binding affinity (−114.0 kcal/mol) among the four metal ions, and a similar trend of binding energies was also found with the CBS-QB3 method (Table S2). The interaction energies calculated with the M06-2X/6-311+G(d) level were found to be in good agreement with the CBS-QB3 method. The Li⁺-ion binding with the prismane molecule (−35.5 kcal/mol) was found to be superior to the binding with the cyclopropane bent bonds (−32.2 kcal/mol) at the same level of theory. The mode of binding differs for prismane as the metal ion binds on the rectangular face, whereas cyclopropanes bind the Li⁺ ion with the edge C−C− bonds.
The binding affinity trend of Li⁺, K⁺, Mg²⁺, and Ca²⁺ ions with the prismane molecule was examined with molecular electrostatic potential (MESP) surfaces. The MESP analysis was performed at the M06-2X/6-311+G(d) level of theory. The minimum electrostatic potential ($V_{\text{min}}$) values show the electron-rich sites in the rectangular face of prismane are given in angstroms.

Figure 1. Optimized geometries of prismane–metal-ion complexes at the M06-2X/6-311+G(d) level. Average distances of metal ions from the carbon of the rectangular face of prismane are given in angstroms.

Figure 2. Calculated MESP surfaces of prismane and metal-ion-bound prismane. Electrostatic potentials computed with an isosurface value of 0.001 au (The blue color specifies the positive potential, and the red color specifies the negative potential; the potential energies are given in kilocalories per mole below the figure).

Figure 3. NCI plot for the prismane molecule and prismane-bound Li⁺, K⁺, Mg²⁺, and Ca²⁺-ion complexes at the M06-2X/6-311+G(d) level of theory.
prismane molecule. The red regions on the rectangular face of prismane indicate probable sites for metal-ion interaction (Figure 2). The binding energies calculated for Li\(^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\) ions with the prismane molecule clearly showed the rectangular face for the preferential binding site (Figures 1 and S1). The adsorption of metal ions on the rectangular face of the prismane molecule dampens further adsorption of such metal ions, and this is revealed in the MESPs, where the negative potentials are vanished (Figure 2).

The K\(^+\) ion binds at a longer distance with prismane of ∼3.0 Å compared to Li\(^+\) (2.2 Å), Mg\(^{2+}\) (2.2 Å), and Ca\(^{2+}\) (2.5 Å). Therefore, Li\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\) ions bind more tightly than K\(^+\) ions. All the metal-ion prismane interaction distances are within the sum of their van der Waals radii (−C···Li\(^+\) = 2.5 Å, −C···K\(^+\) = 3.1 Å, −C···Mg\(^{2+}\) = 2.4 Å, and −C···Ca\(^{2+}\) = 2.7 Å). The MESPs for metal-ion-bound complexes show that Mg\(^{2+}\) has a more positive potential than Li\(^+\), K\(^+\), and Ca\(^{2+}\) ions, which suggests that Mg\(^{2+}\)-complexed prismane would interact more strongly with gas molecules. The binding energy data show that the divalent alkaline earth metals show stronger binding to prismane as compared to alkali metals. The smaller ionic radius of Mg\(^{2+}\) interacts more strongly with the prismane molecule than the relatively larger size of the Ca\(^{2+}\) ion.

The interactions between prismane molecules and metal ions have further been examined with the noncovalent interaction (NCI) plots. NCI plots provide information about the types of interactions such as van der Waals, hydrogen bonding, and steric interactions in the systems. The strength of the interaction is calculated from the sign \((\lambda_2)\); a negative value indicates the attractive interaction, while a positive value indicates the repulsive interaction, and values near 0 indicate weak van der Waals interactions. NCI plots show that there is an increase in both attractive (blue) and repulsive (red) interactions after metal-ion binding to prismane. There is a larger region of attractive interactions in the case of the Li\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\)-bound complexes compared to the K\(^+\)-bound complex, and this corroborates with the trend of their calculated binding energies (Figure 3, Table 1).

These metal-doped prismane complexes were taken for studying the adsorption of flue gas molecules. Carbon dioxide, nitrogen, and methane gases are components of most flue gas streams and chosen for this study. Optimized geometries of all gas-adsorbed complexes are shown in Figure 4, and adsorption energies (ΔE) and free energies (ΔG) of gas molecules with average distances for the interaction between metal ions and gas molecules are given in Table 2. The binding energy and free energy at the CBS-QB3 method are given in Table S3 in the Supporting Information.

In general, the calculated electronic (ΔE) and free energies (ΔG) indicate that the adsorption of gas molecules is feasible.
at ambient temperature (Table 2). Six CO₂ gas molecules can be adsorbed on Ca²⁺-bound prismane d with a favorable binding free energy of ~ −8.7 kcal/mol. Li⁺-bound prismane a can adsorb 3CO₂ molecules with a favorable binding free energy of ~ −3.6 kcal/mol. However, K⁺-bound prismane b can adsorb only one CO₂ molecule. Mg²⁺-bound prismane c can adsorb 4CO₂ molecules with a favorable binding free energy of −19.4 kcal/mol. Similar to CO₂, six N₂ molecules can be adsorbed with Ca²⁺-bound prismane molecule d and five methane gas molecules (Figure 4, d-6N₂ and d-5CH₄). The positive free energy values for N₂ and CH₄ adsorption with b indicate that the adsorption is not feasible at room temperature. Importantly, the interaction of Mg²⁺ is stronger with prismane compared to that of other metal ions; however, the gas adsorption capacity is lower compared to that of the Ca²⁺-bound prismane complex. The calculated desorption energies for all gas-adsorbed complexes show the recycling ability of the gas storage material. The calculated results reveal that the Ca²⁺-bound prismane molecule is superior for adsorbing the flue gas molecules to the Li⁺-, K⁺-, and Mg²⁺-bound prismane molecules. The calculated energy differences of gas molecules with metal-ion-bound prismanes suggest that the separation of CO₂ would be easier from the flue gas mixture. The CBS-QB3 calculated gas adsorption and desorption results corroborate with the M06-2X calculated results that show the superior adsorption of CO₂ gas molecules to N₂ and CH₄ (Table S3). It has been reported that the quadrupole moment plays an important role in gas adsorption and in the separation process.⁴⁹ The difference in the binding affinities of CO₂ and N₂ with the metal–prismane complexes is found because of the larger difference in the electrical quadruple moments of CO₂ (−13.4 ± 0.4 × 10⁻⁹⁸ cm⁴) and N₂ (−4.72 ± 0.26 × 10⁻⁹⁰ cm⁴) gas molecules.⁴⁵ The methane gas molecule does not possess dipole or quadruple moment; however, it has high polarizability, and therefore, the field-induced dipole contributes to its adsorption with the metal complex.⁴⁶ Therefore, the greater permanent electrical quadrupole moment contributes to the higher adsorption of CO₂ gas molecules compared to N₂ and CH₄ gas. The metal-ion-decorated organic systems have been examined for different applications using experimental and computational techniques.⁴⁴–⁴⁶,⁴⁹–⁵¹ Nonetheless, it is also important to gauge the role of counterions in such systems toward their efficacy in the gas adsorption process. We have examined the gas adsorption capacity with a representative system such as the Mg²⁺-decorated prismane molecule in the presence of chloride ions as counterions. The metal ion is divalent in nature, and thus, two chloride ions have been complexed with the Mg²⁺-decorated prismane molecule (Figure S2). The presence of counterions deters the capacity of gas adsorption and reduces to half of the capacity obtained without the presence of counterions at the same level of theory (Table S5).

The theory of atoms in molecules (AIM) is valuable for studying the nature of intermolecular interactions.⁵⁰–⁵² According to the AIM theory, the electron density (ρ) at the bond critical points (BCPs) indicates the strength of the interaction of the bond. The higher the electron density (ρ) value, the stronger would be the bond. The ρ values indicate that the interaction of K⁺ with carbons of prismane (C···K⁺) is relatively weaker and the interaction of Mg²⁺ with carbons of prismane (C···Mg²⁺) is stronger among the studied complexes.⁵³ The values of Laplacian of electron density (V(∇ρ)) are positive in all complexes and indicate that interactions are of the closed-shell type. The ratio of V(∇ρ)/G(r) for all the complexes is in the range between 0.77 and 0.93 and H(∥) > 0 confirms the electrostatic nature of the interaction.⁵⁴,⁵⁵ The binding energy calculations for metal ion–prismane complexes corroborate with the AIM results.

For shared-shell interactions, the potential energy dominates; |W| > G and H are negative; however, in closed-shell-type interactions, the kinetic energy dominates; G > |W| and H are positive.⁵⁶ Therefore, the interaction of all the gas molecules with all the metal ions Li⁺, K⁺, Mg²⁺, and Ca²⁺ was found to be of the closed-shell type Table 3. Another criterion to evaluate the closed-shell type is IV(∥)/G(r) ratio; for the closed-shell type, it is IV(∥)/G(r) < 1, and for the shared-shell interaction, it is IV(∥)/G(r) > 2. In all gas-adsorbed complexes at the BCP for the gas–metal interaction, the IV(∥)/G(r) is found to be less than 1, which further confirms the closed-shell interaction Table 4. It is well known that there is a strong correlation between the electron density at the BCP and the bond energy. Here, the electron density at the BCP between the oxygen atom in CO₂ and the metal is greater as compared to that of

Table 3. Topological Parameters for the Metal–Prismane Bond Calculated with AIM Analysis

| molecule | critical point | electron density(ρ) | G(r) | K(∥) | V(∥) | H(∥) | Laplacian of electron density | IV(∥)/G(r) |
|----------|----------------|---------------------|------|------|------|------|-----------------------------|-----------|
| a        | RCP(C···Li⁺)   | 0.02368             | 0.03467 | −0.00569 | −0.02898 | 0.00569 | 0.16146                     | 0.83585   |
| b        | CCP(C···K⁺)    | 0.01274             | 0.01404 | −0.00314 | −0.01090 | 0.00314 | 0.06872                     | 0.77654   |
| c        | RCP(C···Mg²⁺)  | 0.03402             | 0.04634 | −0.00333 | −0.04301 | 0.00333 | 0.19867                     | 0.92814   |
| d        | BCP(C···Ca²⁺)  | 0.03297             | 0.03382 | −0.00220 | −0.03162 | 0.00220 | 0.14411                     | 0.93485   |

aG(∥) = Lagrangian kinetic energy, K(∥) = Hamiltonian kinetic energy, V(∥) = Potential energy density, and H(∥) = Energy density. RCP (ring critical point), CCP (cage critical point), BCP (bond critical point).
Table 4. Topological Parameters for the Bond between the Gas Molecule and Metal–Prismane Complex Calculated with AIM Analysis

| molecule | critical point | Electron density(ρ) | G(ν) | K(ν) | V(ν) | H(ν) | Laplacian of electron density | η(ν)/G(ν) |
|----------|----------------|----------------------|------|------|------|------|-------------------------------|------------|
| a-1CO₂  | Li⁺···O        | 0.02585              | 0.04189 | -0.01103 | -0.03086 | 0.01103 | 0.21167                     | 0.73671    |
| a-1N₂   | Li⁺···N        | 0.01917              | 0.02503 | -0.00627 | -0.01876 | 0.00627 | 0.12521                     | 0.74954    |
| a-1M    | Li⁺···C        | 0.01787              | 0.02307 | -0.00408 | -0.01899 | 0.00408 | 0.10858                     | 0.82316    |
| b-1CO₂  | K⁺···O        | 0.01586              | 0.01747 | -0.00407 | -0.01341 | 0.00407 | 0.08616                     | 0.76727    |
| b-1N₂   | K⁺···N        | 0.01058              | 0.00942 | -0.00245 | -0.00698 | 0.00245 | 0.04748                     | 0.74039    |
| b-1M    | K⁺···C        | 0.00914              | 0.00794 | -0.00191 | -0.00603 | 0.00191 | 0.03941                     | 0.75900    |
| c-1CO₂  | Mg⁺²···O      | 0.04441              | 0.08077 | -0.01513 | -0.06564 | 0.01513 | 0.38360                     | 0.81268    |
| c-1N₂   | Mg⁺²···N      | 0.03510              | 0.04847 | -0.00726 | -0.04121 | 0.00726 | 0.22291                     | 0.85022    |
| c-1M    | Mg⁺²···C      | 0.03322              | 0.04201 | -0.00235 | -0.03965 | 0.00235 | 0.17743                     | 0.94382    |
| d-1CO₂  | Ca⁺³···O      | 0.03626              | 0.04964 | -0.00780 | -0.04185 | 0.00780 | 0.22976                     | 0.84296    |
| d-1N₂   | Ca⁺³···N      | 0.02508              | 0.02599 | -0.00431 | -0.02168 | 0.00431 | 0.12117                     | 0.83433    |
| d-1M    | Ca⁺³···C      | 0.02288              | 0.02250 | -0.00215 | -0.02035 | 0.00215 | 0.09858                     | 0.90451    |

Table 5. Gravimetric Density for Gas-Adsorbed Complexes Calculated in Weight Percent

| gravimetric density with prismane | Li⁺ | K⁺ | Mg⁺² | Ca⁺³ |
|---------------------------------|-----|----|------|------|
| CO₂                             | 60.82 | 27.30 | 61.22 | 69.1 |
| N₂                              | 39.71 | 19.29 | 52.25 | 58.7 |
| CH₄                             | 15.87 | 12.04 | 31.97 | 40.4 |

Table 6. Electronegativity χ (Electronvolts), Hardness η (Electronvolts), and Electrophilicity ω (Electronvolts) for Li⁺-Gas-Adsorbed Complexes Optimized at the DFT-Based M06-2X/6-311+G(d) Level

| complex | χ (eV) | η (eV) | ω (eV) |
|---------|--------|--------|--------|
| a-1CO₂  | -8.94686 | 7.83513 | 0.430159 |
| a-1N₂   | -3.0979 | 8.3619 | 0.39063 |
| a-1M    | -8.06207 | 8.23743 | 0.36722 |
| b-1CO₂  | -7.87334 | 7.93449 | 0.337349 |
| b-1N₂   | -8.5698 | 8.15616 | 0.410837 |
| b-1M    | -8.46828 | 8.01846 | 0.394388 |
| a-1CO₂  | -8.33558 | 8.57277 | 0.40854 |

Table 7. Electronegativity χ (Electronvolts), Hardness η (Electronvolts), and Electrophilicity ω (Electronvolts) for K⁺-Gas-Adsorbed Complexes Optimized at the DFT-Based M06-2X/6-311+G(d) Level

| complex | χ (eV) | η (eV) | ω (eV) |
|---------|--------|--------|--------|
| b-1CO₂  | -7.94205 | 7.30836 | 0.31675 |
| b-1N₂   | -7.98458 | 7.38693 | 0.323006 |
| b-1N₂   | -7.79571 | 7.59186 | 0.316448 |
| b-1M    | -8.01482 | 7.34589 | 0.323649 |

Table 8. Electronegativity χ (Electronvolts), Hardness η (Electronvolts), and Electrophilicity ω (Electronvolts) for Mg²⁺-Gas-Adsorbed Complexes Optimized at the DFT-Based M06-2X/6-311+G(d) Level

| complex | χ (eV) | η (eV) | ω (eV) |
|---------|--------|--------|--------|
| c-1CO₂  | -15.2846 | 5.6186 | 0.98900 |
| c-2CO₂  | -13.8639 | 7.4029 | 0.9507 |
| c-4CO₂  | -12.7364 | 8.0611 | 0.8969 |
| c-1N₂   | -11.6432 | 8.4942 | 0.7898 |
| c-2N₂   | -10.3489 | 7.6785 | 0.9469 |
| c-4N₂   | -12.7074 | 7.7714 | 0.8607 |
| c-1M    | -13.8664 | 7.2587 | 0.9573 |
| c-2M    | -13.0881 | 7.8335 | 0.9204 |
| c-3M    | -12.2996 | 8.5595 | 0.8881 |

CONCLUSIONS

In this work, we report a detailed study of selective CO₂ adsorption with metal-ion-doped prismane molecules computationally. The CBS-QB3 and M06-2X/6-311+G(d) calculated
results show that one Li⁺, K⁺, Mg²⁺, and Ca²⁺ ion–molecule can bind with each prismane molecule with the favorable binding energy. Such metal-ion-bound complexes were further evaluated with the MESP study and AIM analysis. The MESP plots clearly show the high negative potential on the rectangular face of prismane as the possible site for metal-ion binding, which corroborates with binding energies of the Li⁺ ion with both rectangular and triangular faces. The Mg²⁺ ion can bind strongly (−114.0 kcal/mol) with prismane as compared to Li⁺, K⁺, and Ca²⁺ (−35.5, −16.6, and −79.7 kcal/mole, respectively). The AIM analysis sheds light on the nature of the interaction between prismane and metal ions and suggests that the electrostatic interaction is responsible for the stronger binding for such metal ions. The higher electron density at the BCP of C−Mg²⁺ shows the stronger interaction of Mg²⁺ with prismane compared to the other two metal ions, and these results also corroborate with binding energy results.

In the gas adsorption study, it is observed that CO₂ binds strongly as compared to N₂ and CH₄ with all the metal-doped prismane complexes. The Ca²⁺-bound complex can adsorb six CO₂ molecules with an average binding energy of −181.8 kcal/mol at the M06-2X/6-311+G(d) level of theory. Six N₂ gas molecules and five CH₄ gas molecules can also be bound with the Ca²⁺-bound prismane complex with the average binding energies of −12.6 and −13.4 kcal/mol, respectively. The AIM analysis performed for all gas molecules shows the closed-shell-type interaction between gas molecules and metal-ion-complexed prismane molecules. The interaction of Mg²⁺ is stronger with prismane; however, the gas adsorption capacity is lower compared to that of the Ca²⁺-bound prismane complex. The calculated gravimetric density for the Ca²⁺-bound prismane complex and CO₂ gas molecules (69.1 wt %) was found to be better than those of the known MOFs, many graphene derivatives, and calcium-embedded materials. The stabilities of the gas-adsorbed complexes were confirmed with the chemical hardness and electrophilicity calculations. The difference in the affinity of CO₂ as compared to that of N₂ and CH₄ gas molecules with prismane−Ca²⁺ is ~5 kcal/mol, and therefore, such a material is found to be promising for selective CO₂ adsorption from CO₂, N₂, and CH₄ flue gas mixtures. The CO₂ adsorption capacity and selectivity with a small saturated hydrocarbon system hold great potential for cost-effective CO₂ capture from the flue gas mixture.

### Computational Methodology

All energy calculations and geometry optimization of complexes were performed in the Gaussian09 program. We have used the M06-2X DFT functional as it is considered to be reliable for studying the NCIs and this functional has been employed in recent studies of gas adsorption processes. We have used a triple-split valence basis set with polarization and the diffuse function, which is the 6-311+G(d) basis set. The calculated results are further validated with the higher method CBS-QB3 for increased accuracy. The average adsorption energies (ΔE_ads) were calculated as

$$\Delta E_{\text{ads}} = \frac{E[nG - \text{complex}] - E[\text{complex}] - E[nG]}{n}$$

where $E[nG - \text{complex}]$, $E[\text{complex}]$, and $E[nG]$ are the energies of $nG$ molecules adsorbed on the prismane−metal-ion complex, the prismane−metal-ion complex, and $nG$ molecules, respectively. Harmonic frequency calculations are performed to validate the minima of the optimized complexes with no imaginary frequency. The free energies of gas adsorption (ΔG) are calculated with the following formula

$$\Delta G_{\text{ads}} = \frac{FE[nG - \text{complex}] - FE[\text{complex}] - FE[nG]}{n}$$

where $FE[nG - \text{complex}]$, $FE[\text{complex}]$, and $FE[nG]$ are the free energies of $nG$ molecules adsorbed on the prismane−metal-ion complex, the prismane−metal-ion complex, and $nG$ molecules, respectively.

The maximum number of gas molecules adsorbed was computed with the sequential addition of one gas molecule in the metal ion−prismane complex. The complex containing the maximum number of gas molecules with favorable free-energy values suggests the feasibility of the adsorption process.

Desorption energies were calculated with

$$\Delta E_{\text{des}} = E[\text{gas}] + \frac{1}{m}(E_{n-m} - E_n)$$

where $E[\text{gas}]$ is the energy of the gas molecule, $m$ is the number of gas molecules desorbed, and $n$ is the total number of the gas molecules absorbed.

Gravimetric density (W) is calculated with the following formula in weight percent

$$W = \frac{M_{\text{gas}}}{(M_{\text{gas}} + M_{\text{complex}})} \times 100\%$$

where $M_{\text{gas}}$ is the mass of the number of gas molecules adsorbed and $M_{\text{complex}}$ is the mass of the metal ion−prismane complex.

AIM calculations were examined in MULTIWFN-3.2.1 software with the wave functions generated from GAUSSIAN 09. The MESP was generated with Molekel software. Chemical hardness ($\eta$) and electrophilicity ($\omega$) values were calculated with the following formulas

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}$$

$$\chi = \frac{1 + A}{2} \approx \frac{E_{\text{HOMO}} - E_{\text{LUMO}}}{2}$$

$$\eta = \frac{1 - A}{2} \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

### Table 9. Electronegativity $\chi$ (Electronvolts), Hardness $\eta$ (Electronvolts), and Electrophilicity $\omega$ (Electronvolts) for Ca²⁺-Gas-Adsorbed Complexes Optimized at the DFT-Based M06-2X/6-311+G(d) Level

| complex | $\chi$ (eV) | $\eta$ (eV) | $\omega$ (eV) |
|---------|-------------|-------------|--------------|
| d       | −13.8222    | 6.71517     | 0.879947     |
| d-1CO₂  | −13.103     | 7.02945     | 0.827757     |
| d-2CO₂  | −12.341     | 7.68663     | 0.802936     |
| d-4CO₂  | −11.3775    | 8.2683      | 0.735697     |
| d-6CO₂  | −10.9558    | 8.11188     | 0.667808     |
| d-1N₂   | −13.311     | 7.02864     | 0.856718     |
| d-2N₂   | −12.8323    | 7.52922     | 0.850356     |
| d-4N₂   | −12.1056    | 7.50141     | 0.753975     |
| d-6N₂   | −11.986     | 7.53435     | 0.742395     |
| d-1M    | −13.2628    | 7.05213     | 0.850812     |
| d-2M    | −12.7121    | 7.56648     | 0.838636     |
| d-4M    | −11.8022    | 8.47098     | 0.809292     |
where $\chi$ is the electronegativity, $\mu$ is the electronic chemical potential, and $I$ and $A$ represent the ionization potential and electron affinity of the system, respectively. Here, $I$ is calculated as the negative value of HOMO energy and $A$ as the negative value of LUMO energy as this approximation is validated\(^7\) and used in similar gas adsorption studies.\(^73\)–\(^75\)

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04299.

Li$^+$-ion binding with multiple sites on prismane; Li$^+$ ion binding energies ($\Delta E$) in kilocalories per mole with prismane; metal-ion binding energies ($\Delta E$) and free energies ($\Delta G$) with prismane at CBS-QB3 in kilocalories per mole; average adsorption energies ($\Delta E$), desorption energies ($\Delta D_{E}$), and free energies ($\Delta G$) of gas molecules with prismane–metal complexes at CBS-QB3 in kilocalories per mole; gravimetric density for gas-adsorbed complexes calculated in weight percent; average adsorption energies ($\Delta E$) of gas molecules with prismane–metal complexes in presence of counter ions at M06-2X/6-311+G(d) in kilocalories per mole; and optimized geometries of gas-adsorbed complexes with counterions at the M06-2X/6-311+G(d) level (PDF)

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**Notes**

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