Activation of Small Molecules (H₂, CO₂, N₂O, CH₄, and C₆H₆) by a Porphyrinoid-Based Dimagnesium(I) Complex, an Electride

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Supporting Information

ABSTRACT: A density functional theory-based computation has been carried out to reveal the geometrical and electronic structures of Mg₂EP (1), where EP is an extended (3.1.3.1) porphyrinoid system. EP is a 22 π electronic system and is aromatic in nature. Here, we have studied the thermodynamic and kinetic stabilities of EP²−-supported Mg₂²⁺ ion. The nature of bonding has been studied using natural bond orbital and atoms in molecules schemes. The presence of a covalent Mg(I)–Mg(I) σ-bond in Mg₂EP is confirmed. The occurrence of a non-nuclear attractor (NNA) with large electron population, negative Laplacian of electron density at NNA, and presence of an electron localization function basin along with large nonlinear optical properties prompt us to classify Mg₂EP as the first porphyrinoid-based organic electride. Further five small molecules, viz., dihydrogen (H₂), carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄), and benzene (C₆H₆), are found to be activated by the electron density between the two Mg atoms in Mg₂EP.

INTRODUCTION

Magnesium (Mg) at its +1 oxidation state in a stable Mg–Mg bond has been detected in HMgMgH by spectroscopic technique at low-temperature gas matrices.¹ ² However, a complete laboratory synthesis of stable Mg(I)–Mg(I) bonded complexes was reported by Green et al. in 2007.³ This work reported the syntheses of [Mg(DippPriso)]₂; DippPriso = [(DippN)₂CNPr₂]; Dipp = 2,6-diisopropylphenyl, Pr = isopropyl and [Mg(DippNacnac)]₂; DippNacnac = [(Dipp)NC(Me)₂]CH complexes, where a Mg(I)–Mg(I) σ-bond is confirmed by computational studies. After this work, stabilizing Mg atoms at the +1 oxidation state became a state-of-the-art research arena for chemists. The common synthetic strategy involved is to design and synthesize bulky ligands that can stabilize Mg⁺⁺⁺ entity in its cavity. A large number of complexes with stable Mg(I)–Mg(I) σ-bond have been synthesized by experimentalists, and computational studies have been carried out by theoreticians to predict such stable complexes.⁴–⁶

Porphyrins are one of the important classes of macrocycles, where four pyrrole units are connected alternately through methine (=CH–) linkers.⁷ The 18 conjugated π-electrons (14n + 2) π-electrons; n = 4) present in the porphyrins make it highly aromatic.⁸–¹¹ The deprotonated free base porphyrins can form complexes with metal atoms; they are known as metalloporphyrins, which are fundamental units of a number of biomolecules without which life on this earth cannot survive.¹²¹³ The core of the porphyrin has been extended and stretched using bridging atoms.¹⁴–¹⁷ These modified porphyrinoid cores have strong red-shifted UV–vis absorption that has potential applications in photochemistry as photosensitizers.¹⁸¹⁹ The stretched porphyrinoid cores can be used as ligands for the generation of unusual metalloderivatives.²⁰ In 1990, [22]octaethylporphyrin(3.1.3.1) has been synthesized where the inner ring of the porphyrin unit has been extended by four carbon atoms.²¹²² This extended porphyrin has 22 π-electrons (follows Hückel’s (4n + 2) rule, n = 5) and hence is aromatic in nature.²³

Here, the extended (3.1.3.1) porphyrin (without any substitution, denoted EP), HEP, has been considered as a ligand that can stabilize MgEP⁺⁺ ion in Mg₂EP as shown in Scheme 1a. The bonding modes of the “Nacnac” ligand can be mimicked by the EP²−; see Scheme 1b. In the [Mg{Nacnac}]₂ complex, the two ligands are not connected and oriented almost perpendicular to each other.³ However, the EP²− is planar and cyclic. So, it will be interesting to study the Mg₂EP complex and explore its nature of bonding and other properties.

Electrides are a class of ionic compounds that have trapped electrons as anions. These loosely bound electrons in electrides result in high nonlinear optical (NLO) properties¹⁹,²² and accordingly are useful as in reversible H₂ storage material,²³ in electron emitter,²⁴ and in activation of small molecules.²⁵,²⁶ In 1983, Dye et al. synthesized the first crystalline organic electride, Cs⁺(18-crown-6)Cs–,²⁷ which influenced them to...
synthesize a series of such compounds. In 2005, Na+(tri-pip-aza-2.2.2)− was synthesized by Redko et al. The first synthesized crystalline inorganic electride is [Ca24Al28O64]4+·(4e−), where the unit cell vacancies hold the trapped electrons. The stability and hence the practical applications of electrides depend on their sensitivity toward air and temperature.

Density functional theory (DFT)-based computations have been performed and thermodynamic parameters have been calculated to check the stability of the Mg2EP complex. Complete bonding analyses have been performed with the help of natural bond orbital (NBO) and atoms in molecules (AIM) schemes. The kinetic stability of the complex has also been studied using the ab initio molecular dynamics. The bowl inversion of the central "Mg2N4H2" unit has been observed. Furthermore, the electronegativity of Mg2EP has been elucidated. Small molecules like H2, CO2, N2O, CH4, and C6H6 are found to be activated followed by dissociation of H−H, C−O, N−O, aliphatic C−H, and aromatic C−H bonds, respectively, by the Mg2EP. Stable complexes are formed with bridging ligands between the two Mg atoms.

**COMPUTATIONAL DETAILS**

The geometry optimizations in this study have been performed at the M06-2X-D3/6-311+G(d,p)32−34 level of theory. Frequency calculations are also carried out at the same computational level to ensure that the optimized structures are at the minima on their respective potential energy surfaces. The M06-2X functional is well known for its wide and accurate predictive applications involving main group thermochemistry. The dynamical behavior of the Mg2EP has been studied using an atom-centered density matrix propagation (ADMP)35−38 technique. In this ADMP simulation, we have evolved the optimized Mg2EP at 298 and 500 K temperatures at 1 atm pressure. We have simulated the Mg2EP system over a total time length of 1 ps with 2 fs time interval. We have used the Gaussian 16 program package for the calculations.

The natural population analysis is carried out to get natural charges on the atoms, and the Wiberg bond indices (WBIs) are computed to obtain the bond order between any atomic pair using the natural bond orbital (NBO) scheme at the M06-2X-D3/6-311+G(d,p) level of theory. We have also compared the NBO results of Mg2EP at the M06-2X-D3 level with that obtained at the MP2/6-31G(d,p) level of theory (denoted MP2/6-31G(d,p)) level of theory. The natural population analysis has been carried out using NBO 3.146 as implemented in Gaussian 16.

The topological descriptors of the electron density have been computed at DFT and MP2 levels with the help of Multiwfn software. Basin analyses based on the electron density (ρ(r)) and the electron localization function (ELF) have been performed. The localization index (λ) and delocalization index (δ) based on the ELF basin have been computed. It is termed as “basin” following these references.

Average linear polarizability (α̅), first hyperpolarizability (β), and second hyperpolarizability (γ∥) were calculated at the B3LYP/6-31+G(d) level, where the 6-31+G(d) basis set is used for Mg atoms and the 6-31+G basis set is used for all other atoms. We have used the following equations to calculate α̅, β, and γ∥.

\[
\alpha = \frac{1}{3} \sum_{i=x,y,z} \alpha_{ii}
\]

**Scheme 1. Schematic Representations of (a) the Stabilization Path for the Mg2EP Complex and (b) Structural Similarity between the Nacnac and EP2− Ligands**

![Scheme 1](image-url)
Results and Discussion

Structure and Energetics. The minimum energy geometry of Mg₂EP (1) at the M06-2X-D3/6-311+G(d,p) level has been presented in Figure 1. The optimized geometry of 1 is nonplanar and found to be in the C₁v point group of symmetry. The Mg–Mg bond length in 1 is 2.787 Å. Pyykko et al.⁵ have predicted the Mg–Mg single bond length to be 2.780 Å, which is in good agreement with our computed value. The four Mg–N bond lengths are equal in 1, and it is 2.062 Å. We have also optimized the geometry of 1 at the B3LYP/6-311+G(d,p) level. The rMg-Mg and rMg-N are found to be 2.792 and 2.075 Å, respectively. Thus, we can say that the result is not an artifact of using a particular computational level. The four N atoms of the EP²⁻ ligand in 1 form a rectangle (denoted N4-plane), and the two Mg atoms are above that plane and in the same side of this N4-plane. The distance between the center of two Mg atoms and the center of the N4-plane is 0.661 Å at M06-2X-D3 and 0.672 Å at B3LYP levels. Scheme 1 has been considered to find out the thermochemical stability of 1 at 298 K temperature and 1 atm pressure. The Gibbs’ free energy change (ΔG) for the formation of 1 is ~83.9 kcal/mol, which indicates that the formation of 1 is a thermochemically favorable process (see Scheme 1a). Further, the dissociation of 1 into Mg²⁺ and EP²⁻ fragments is thermochemically nonspontaneous as ΔG₂ is 515.9 kcal/mol.

A planar transition state (TS₁₋₁) has been identified and optimized corresponding to the inversion of the two Mg atoms with respect to the N4-plane in 1. The point group symmetry of TS₁₋₁ is C₂v. The Mg–Mg distance in TS₁₋₁ is 2.652 Å at M06-2X-D3 and 2.664 Å at B3LYP levels. The imaginary frequency is 148 (137) cm⁻¹ at the M06-2X-D3 (B3LYP) level. All four Mg–N bond lengths are equal to each other, and it is 2.026 (2.039) Å at the M06-2X-D3 (B3LYP) level. Geometry 1 goes through this TS₁₋₁, and the Mg₂N₄H₂ unit gets inverted, that is, the two Mg atoms (and two H atoms of the opposite side of the N4-plane) go to the other side of the N4-plane through the planar TS₁₋₁ akin to that in NH₃ inversion. The Gibbs’ free energy barrier (ΔG) for the inversion of the Mg₂N₄H₂ unit is found to be 5.8 (5.2) kcal/mol at the M06-2X-D3 (B3LYP) level. Figure 2a represents a complete “bell-shaped” IRC path that connects the two conformers of 1 and TS₁₋₁.

The ab initio molecular dynamics study has been performed to reveal the dynamical behavior of 1. The optimized Mg₂EP has been simulated to evolve using the ADMF method over 2 ps of time at 298 and 500 K temperatures. The time evolution of the total energy at both the temperatures is shown in Figure 2b. The total energy at 500 K temperature is higher than that at 298 K, as expected. The oscillations in the energy curves have been observed at both the temperatures. This may be due to an increase in the nuclear kinetic energy changes arising out of the structural deformations of 1. The changes in the Mg–Mg (Δr(Mg–Mg), Å) and Mg–N (Δr(Mg–N), Å) bond lengths with respect to their optimized values in 1 (i.e., geometry at t = 0) against time have been plotted. To keep
track of the dynamics, two Mg atoms and four N atoms have been marked as shown in Figure S1a. The plots in Figures 2c and S1b show that Mg–Mg and Mg–N bond lengths fluctuate around their optimized values all throughout the simulations at both the temperatures, but they do not disintegrate. These two observations reveal the kinetic stability of the Mg2EP. The inversion of the central Mg2N4H2 unit at 500 K may be clearly understood from the plots in Figure 2d. Here, we have calculated the $d_{\text{Mg}}$ ($d_{\text{Mg}}$ = distances between the center of the two Mg atoms and the center of the four N atoms, with proper sign) and $d_{\text{H}}$ ($d_{\text{H}}$ = distances between the center of the two H atoms and the center of the four N atoms, with proper sign) at both the temperatures throughout the overall simulation and plotted it against time. The plot clearly shows an inversion of the $d_{\text{Mg}}$ and $d_{\text{H}}$, which indicates the inversion of the two Mg and two H atoms at 298 and 500 K.

**Figure 2.** (a) IRC plot corresponding to the inversion of I through TS1. The plot of (b) total energy against time, (c) change in the $r_{\text{Mg–Mg}}$ and $r_{\text{Mg–N}}$ bond lengths with respect to the optimized I ($t = 0$) against time, and (d) $d_{\text{Mg}}$ and $d_{\text{H}}$ against time at 298 and 500 K.

**Nature of Bonding in I. Molecular Orbital (MO) Diagram.** Molecular orbital analysis has been carried out on I at the M06-2X-D3/6-311+G(d,p) level. The shapes and energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have been presented in Figure 4. The shape of the LUMO represents a $\pi$-orbital, distributed over the EP2$^-$ ligand. The HOMO represents the Mg–Mg $\sigma$ bond. The 3s and 3p atomic orbitals on each Mg atom are the major contributors, and they contribute 26.0 and 15.4%, respectively, toward the formation of the Mg–Mg $\sigma$ bond. The contribution from other atoms toward HOMO is less than 5%. The energy difference between the HOMO and the LUMO is 3.18 eV.

**Natural Bond Orbital (NBO) Analysis.** The natural charge on the Mg and N atoms and the Wiberg bond index (WBI) values for the Mg–Mg and Mg–N bonds in I at the M06-2X-D3/6-311+G(d,p) level are presented in Table 1.

The natural charges on each of the Mg and N atoms are 1.01 and $-0.80$ le/, respectively. The WBI value for the Mg–Mg bond is 0.647, which suggests the presence of a single bond between the two Mg atoms. The WBI value for the Mg–N bonds is 0.081 in Mg2EP, suggesting that the interaction between the Mg and N atoms is noncovalent in nature. The NBO results at the MP2 level also support the same
arguments. The Mg−Mg bond orbital has been generated at the MP2 level and is shown in Figure S2. The occupancy of Mg−Mg bond orbital is 1.79 |e|.

The atom orbital contributions from the two Mg atoms are equal, indicating that the Mg−Mg bond is nonpolar in nature. The contributions from the 3s and 3p atomic orbitals are 92.1 and 5.9%, respectively, toward the Mg−Mg bond orbital, whereas the 3d orbital contributes only 1.6%.

Electron Density Analysis. Different topological parameters based on the electron density at relevant critical points (CPs) of 1 have been computed at both MP2 and DFT levels and are presented in Table 2. The molecular graph of the MgEP is shown in Figure 5a. The molecular graph at the MP2 and DFT methods are the same. A non-nuclear attractor (NNA; (3, −3)-type critical point) has been located close to the middle of the two Mg atoms. The presence of NNA in dimeric Mg(I) complexes has been confirmed experimentally. The electron density (ρ(rc)) at this NNA is 0.034 au at the MP2 level. The Laplacian of electron density (∇^2ρ(rc)) at the NNA is −0.043 au. The negative ∇^2ρ(rc) indicates the electron accumulation between the two Mg atoms. The population of the NNA basin is 1.03 electrons with 46% of localization. Two NNA−Mg bond paths are found, connecting the NNA and the two Mg atoms. The ρ(rc) values at the NNA−Mg bond critical points (BCPs) are 0.032 au and the ∇^2ρ(rc) values are 0.009 au. The energy density (H(rc)) values are negative. The DFT-level calculations have predicted almost similar results. Figure 5b,c shows a distinct region between the two Mg atoms where electron density is accumulated. An ELF basin between the two Mg atoms, C(NNA), is identified (see Figure 5d,e) with a population of 1.78 electron in it with 61% localization at MP2/
aV(D+T)Z level of theory. On the basis of these results, we can say that there is a considerable amount of covalency in the bond between the two Mg atoms. The positive $\nabla^2 \rho(r_c)$ and $H(r_c)$ and low $\delta$ values indicate that the Mg–N interactions are noncovalent in nature. Two NNA–H bond paths have been found. The low $\rho(r_c)$ and positive $\nabla^2 \rho(r_c)$ and $H(r_c)$ values suggest that the interaction is weak.

Nonlinear Optical (NLO) Property of 1. Average linear polarizability ($\bar{\alpha}$), first hyperpolarizability ($\beta$), and second hyperpolarizability ($\gamma_\parallel$) have been calculated for 1 and are presented in Table S1. The $\bar{\alpha}$, $\beta$, and $\gamma_\parallel$ values are 493.7, $3.62 \times 10^{2}$, and $1.1 \times 10^{5}$ au, respectively. Further, we have

| CP type | $\rho(r_c)$ | $\nabla^2 \rho(r_c)$ | $G(r_c)$ | $V(r_c)$ | $H(r_c)$ | N(pop) | LI | % LI | $\delta$ |
|--------|-------------|---------------------|----------|---------|---------|--------|----|------|--------|
| NNA (3, −3) | 0.034 | −0.043 | 0.001 | −0.012 | −0.011 | 1.03 | 0.47 | 46 |
| (0.030) | −0.034 | (0.001) | −0.011 | (0.010) | (0.68) | (0.20) | (30) |
| (0.031) | −0.036 | (0.001) | −0.011 | −0.010 | (0.71) | (0.22) | (31) |
| NNA–Mg (3, −1) | 0.032 | 0.009 | 0.011 | −0.020 | −0.009 | 0.35 |
| (0.030) | 0.009 | (0.007) | −0.016 | (0.009) | (0.31) | (0.32) |
| (0.031) | −0.010 | (0.007) | −0.016 | −0.009 | (0.04) | (0.05) |
| NNA–H (3, −1) | 0.015 | 0.013 | 0.005 | −0.006 | −0.001 | 0.07 |
| (0.013) | 0.013 | (0.004) | −0.005 | −0.001 | (0.04) | (0.05) |
| (0.014) | 0.012 | (0.004) | −0.005 | −0.001 | (0.04) | (0.05) |
| Mg–N (3, −1) | 0.047 | 0.305 | 0.072 | −0.068 | 0.004 | 0.16 |
| (0.045) | 0.300 | (0.067) | −0.060 | 0.008 | (0.20) | (0.20) |
| (0.044) | 0.285 | (0.064) | −0.056 | 0.008 | (0.20) | (0.20) |

The values without parentheses, within second brackets, and within square brackets indicate the values calculated at MP2/aV(D+T)Z, B3LYP/6-311++G(d,p), and M06-2X-D3/6-311+G(d,p) levels, respectively.

Figure 5. Topological analysis of 1. (a) Molecular graph. (b) Three-dimensional (3D) surface plot of $\nabla^2 \rho(r_c)$; isosurface value = −0.001; (c) two-dimensional (2D) plot of $\nabla^2 \rho(r_c)$; the blue and green lines indicate $\nabla^2 \rho(r_c) > 0$ and $\nabla^2 \rho(r_c) < 0$ regions, respectively. (d) Three-dimensional (3D) surface plot of ELF; isosurface value = 0.800. (e) Two-dimensional (2D) plot of ELF.
compared the $\alpha$, $\beta$, and $\gamma$ values of 1 with the corresponding previously reported values for Li@Calix, Na@Calix, Li@B10H14, Li4(TCNQ), and Na4(TCNQ).68 The results show that Mg2EP has the largest $\alpha$ value among all of them. However, the $\beta$ and $\gamma$ values of 1 are smaller as compared to those in the other systems, albeit sufficiently high. Thus, 1 can be treated as an NLO material.

**Electride Property of 1.** Classification of a molecule as an electride is based on several properties, viz., large nonlinear optical properties, presence of a non-nuclear attractor (NNA) of the electron density, electron localization function (ELF) basins, and noncovalent index (NCI), which have to be computed by reliable and sophisticated methods. The AIM results have confirmed the presence of an NNA with a negative $\nabla^2\rho(r)$ value, with a large electron population in it (see Table 2). The ELF analysis showed that the C(NNA) has 1.78 electron population with 61% localization in it. The high polarizability and first and second hyperpolarizabilities also suggest the NLO behavior of 1. The green region in the NCI plot (see Figure S3) shows the electron localization between the two Mg atoms in 1. All these results strongly establish that 1 can be classified as an organic electride, and it is the first electride having a porphyrinoid moiety.

**Activation of Small Molecules.** Activation and dissociation of small gas molecules, especially greenhouse gases like carbon dioxide (CO$_2$) and nitrous oxide (N$_2$O), have been considered to be the need of the hour. This provides a two-pronged benefit, viz., it can remove the hazardous global warming gases and it provides chemical precursors to various chemical reactions. Activation of the C–H bonds in organic molecules is one of the most challenging jobs for chemists. Finding cheap, selective, and efficient catalysts that can activate and eventually dissociate both aliphatic and aromatic C–H bonds has been considered to be a great challenge. Electrides are found to activate small molecules like CO$_2$ and N$_2$, and they have been used for reversible storage of molecular dihydrogen (H$_2$).24,66 Here, we have studied the activation followed by dissociation of five small molecules, viz., H–H bond in H$_2$, C–O bond in CO$_2$, N–O bond in N$_2$O, and C–H bond in methane (CH$_4$) and benzene (C$_6$H$_6$) molecules using Mg$_2$EP, as shown in Scheme 2.

**Mechanistic Investigation of Hydrogenation of H$_2$.** Direct hydrogenation of dimeric Mg(I) complexes has not been achieved experimentally till now.67 The kinetic stability of Mg(I) dimer is suggested as the possible reason for the inertness of these complexes.68 Computations at the B3LYP/6-31G(d) level have shown that the hydrogenation of guanidinate-supported Mg$_2$ complexes producing the corresponding bridged hydrido (µ-H) complexes are exothermic in nature ($\Delta H = -24$ kcal/mol).69 An indirect hydrogenation process for the Mg(I) dimers, using aluminum(III) hydride has been achieved.70 Complex 1 has been subjected to hydrogenation, which leads to the product Mg,EP(µ-H)$_2$ (denoted 4, in Figure 6). The hydrogenation process is exothermic by $\Delta H = -33.4$ kcal/mol and exergonic by $\Delta G = -25.1$ kcal/mol. Thus, the hydrogenation process is thermochemically spontaneous. The hydrogenation of 1 is found to be a stepwise process, and the complete reaction path is shown in Figure 6.

At the early step of the reaction, 1 forms a prereaction complex, 2, with one H$_2$ molecule. Then, it generates a transition state, TS$_{2-3}$, where the Gibbs' free energy barrier is 31.8 kcal/mol with respect to 2. The H–H bond length in the free H$_2$ molecule is 0.740 Å (see Figure S4), which is increased by 0.006 Å in 2, which further increased to 1.124 Å in TS$_{2-3}$ (see Table S2). Then, the structure TS$_{2-3}$ moves to the intermediate 3, where the H–H bond is completely dissociated ($r_{H-H} = 2.940$ Å). One H atom is bonded to two Mg atoms, forming a hydrido bridge, whereas another is only bound to one Mg atom in 3. Structure 3 is stabilized by $-1.4$ kcal/mol of Gibbs’ free energy as compared to that of 1 and one H$_2$ molecule. But, it then reorganizes itself toward a more stable geometry, 4. The bridged H atom moves inward to the N4-plane. Another TS$_{3-4}$ is formed, which has 2.9 kcal/mol more free energy than 3. The structural parameters of 3 and TS$_{3-4}$ are almost similar, except the bent of the µ-H. The bent of the µ-H in 3 is outward, which becomes inward in TS$_{3-4}$. At last, it forms the final product 4 with a total gain in free energy of $-25.1$ kcal/mol. The HOMO of TS$_{2-3}$ corresponds to the interaction between the Mg–Mg σ-bond orbital of 1 and the $\sigma^*$-orbital of the H$_2$ molecule (see Figure S5). The activation of the H$_2$ molecule is indicated by the elongated H–H bond length in TS$_{2-3}$. The charges on the H atoms of H$_2$ molecules are $-0.36$ and $-0.48$ lel (see Table S2), making a total of $-0.84$ lel electronic charge on the H$_2$ molecule in TS$_{2-3}$. This indicates a transfer of electron density from 1 to the H$_2$ molecule. The WBI$_{H1-H2}$ values are 1.000 in free H$_2$, which is

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**Figure 6.** Relative free energy (in kcal/mol) profile for H$_2$ activation by 1 calculated at the M06-2X-D3/6-311+G(d,p) level of theory. The sum of the Gibbs' free energies of 1 and H$_2$ ($\Delta G = 1544.39913162$ au) is considered as 0.0 kcal/mol.

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**Scheme 2.** Schematic Representation of the Reactions of H$_2$, CO$_2$, N$_2$O, CH$_4$, and C$_6$H$_6$ Molecules with 1.
decreased to 0.294 in TS2–3; this indicates the weakening of the H–H bond by the population of the $\sigma^*$-orbital of the H2 molecule. In 3, the H2 molecule is completely dissociated, and WBIH–H is 0.008 only. Structure 4 has two hydrides bridged between the two Mg atoms. The Mg–H bond lengths are 1.855 and 1.850 Å. The Mg–Mg distance in 4 is 2.665 Å, which is smaller than that in 1.

### Mechanistic Investigation of CO2 Reactivity

Previous studies have shown that LMMgL type of complexes can effectively activate and dissociate CO2, forming an oxo-bridged ($\mu$-O) complex, which finally gives a carbonate complex. System 1 effectively activates CO2 and forms an oxo-bridged ($\mu$-O) complex with the TS having almost equal energy barrier has been identified earlier, where the Mg atoms were stabilized using tripodal diimine-enolate ligands. The C–O bonds are elongated to have bond lengths of 1.189 and 1.157 Å, and the C=O becomes bent to 161.7°. The TS5–6 transforms to a symmetric intermediate 6, which is stabilized by $−30.6$ kcal/mol. The activation of CO2 requires a transformation from a linear to a bent geometry. The $\angle$COO is 125.1°, and the $r_{C=O}$ is 1.269 Å. The bent $\angle$COO indicates the presence of activated CO2 in TS5–6 and 6. The HOMO of TS5–6 corresponds to the interaction between the Mg–Mg $\sigma$-bond orbital (HOMO) of the MgEP and the LUMO of the CO2 molecule (see Figure S5). The total charge on the CO2 fragment in TS5–6 is $−0.67$ lel. Thus, the flow of electron density from 1 to the CO2 molecule is confirmed. The total charge on the CO2 fragment is $−1.56$ lel in 6. The main contribution to HOMO $−2$ of 6 comes from HOMO of CO2 (see Figure S6). The WBI$^{Mg–Mg}_C$ value is decreased to 0.517 in TS5–6 and to 0.016 in 6 as compared to that in 1. Thus, no Mg–Mg bond is present in 6. The low WBI$^{Mg–C}_C$ values suggest the weakening of the C–O bonds in TS5–6 and 6 (see Table S2).

Although 6 is a stable complex, it dissociates into 9 and CO via the intermediates 7 and 8 and transition states TS6–7 and TS7–8. Transition state TS6–7 leads to the formation of 7 from 6. Transition state TS8–9 has been optimized, which has 6.1 kcal/mol more free energy than that of 7. Finally, TS7–8 leads to 8, which is an adduct of complex 9 and CO. This 9 is an oxo ($\mu$-O) bridged complex, which has one Mg–O–Mg moiety. Further, compound 9 grabs another CO2 molecule and forms adduct 10. Then, 10 forms TS10–11, which finally leads to carbonate complex 11.

### Mechanistic Investigation of N2O Reactivity

N2O comprises only 6% of the total greenhouse gases and has 296 times of the global warming potential (GWP) as compared to that of CO2 (81% of the total greenhouse gases). N2O has 121 years of atmospheric lifetime, which is also much higher than that of CO2. viz., 30–95 years. N2O is thermodynamically stable and is often used as an oxygen transfer agent in organometallic chemistry. Here in this study, we have used N2O to react with 1, which ends up in forming an oxo-bridged complex 9. The complete reaction profile along with the TSs and intermediates are depicted in Figure 8. First, N2O binds to 1, which forms an oxo-bridged complex. The complete reaction profile along with the TSs and intermediates are depicted in Figure 8. First, N2O binds to 1 and forms a prereaction complex 12. The $\Delta G$ for the formation of 12 is 0.3 kcal/mol. A transition state TS12–13 has been found to have 10.2 kcal/mol higher energy as compared to 12. The linear N2O becomes bent in TS12–13. The $\angle$O–N–N is 161.7°, and the N–O and N–N bond lengths in TS12–13 are increased by 0.076 and 0.009 Å, respectively, as compared to that in free N2O. The inspection of the HOMO of TS12–13 reveals the interaction between the HOMO of 1 with the LUMO of N2O (see Figure S5). The total charge of N2O is $−0.26$ lel, which suggests that the direction of the flow of the electron density is 1 to N2O. The TS12–13 then transforms into intermediate 13, which is stabilized by $−35.4$ kcal/mol of free energy. The N–O and N–N bond lengths are 1.370 and 1.219 Å, respectively, and the $\angle$O–N–N is 121.0° in 13. The total charge of N2O is $−1.64$ lel in 13. The HOMO $−2$ of 13 looks like the HOMO of N2O2$^{−}$, indicating the presence of N2O2$^{−}$ fragment (see Figure S6). At last, 13 gains 14.8 kcal/mol energy and forms TS13–14, which leads to the removal of one N2 molecule in the
The N–O bond length in TS$_{13-14}$ is elongated as compared to that in 13, whereas the N–N bond length is decreased in TS$_{13-14}$. The van der Waals complex 14 has been identified; here, the oxo-bridged N$_2$ molecule is bound very loosely. The total stabilization energy of 14 is $-122.1$ kcal/mol. At last, 14 removes the N$_2$ molecule, and complex 9 is found.

Mechanistic Investigation of CH$_4$ Reactivity. Methane, the smallest member of the alkane family, has 84 times more GWP than that of CO$_2$. The complete reaction path for CH$_4$ activation is shown in Figure 9, which looks like the H$_2$ formation reaction profile. The free energy change for the formation of the prereaction complex, 15, is 2.4 kcal/mol. A transition state TS$_{15-16}$ has been formed with a gain of 41.1 kcal/mol energy as compared to 15. Here, we would like to mention that recently high energy barriers for C–H bond activation in CH$_4$ using transition-metal complexes have been reported.$^{81}$ The C–H bond length in free CH$_4$ is 1.089 Å, and the WBI$_{C–H}$ is 0.958. The C–H bond in TS$_{15-16}$ is elongated to 1.593 Å with a decrease in the WBI$_{C–H}$ value to 0.245 (see Table S2). Thus, the C–H bond is activated at 16. The HOMO of the TS$_{15-16}$ corresponds to the interaction between the HOMO of 1 and LUMO of CH$_4$ (see Figure S5). The charge distribution shows that only the C atom and H atom corresponding to the elongated C–H bond differs as compared to that in the free CH$_4$. The H atom acquires negative charge on it, and the charge on the C atom becomes more negative as compared to the free CH$_4$. The total charge on CH$_4$ is $-0.94$ e, indicating a charge donation from 1 to CH$_4$. The TS$_{15-16}$ transforms to the intermediate 16. Here, the C–H bond under consideration is dissociated. The H atom formed a bridge between the two Mg atoms, and the CH$_3$ group is connected to one Mg atom. Then, 16 reorganizes to its final geometry Mg$_2$EP($\mu$-CH$_3$)($\mu$-H), 17, through the transition state TS$_{16-17}$. The geometrical and electronic parameters of the intermediate 16 and TS$_{16-17}$ are almost the same except for the orientation of the bridged H atom. The outward orientation of $\mu$-H becomes inward in TS$_{16-17}$. At last, complex 17 has been formed with one $\mu$-H and one $\mu$-CH$_3$ bond. The total gain in free energy is $-18.3$ kcal/mol, indicating the spontaneity of the complete process, and it is the driving force for the reaction.

Mechanistic Investigation of Benzene Reactivity. Activation of an aromatic C–H bond is one of the tough challenges for organic chemists. We have considered the C–H bond of benzene to get activated using 1. The complete reaction profile for the C–H bond activation is shown in Figure 10. Benzene forms a prereaction complex, 18. The $\Delta G$ for the formation of 18 is $-3.7$ kcal/mol. Benzene is bound to 1 with weak van der Walls interaction between them. This complex 18 then undergoes a structural change and forms TS$_{18-19}$ with a gain of 39.9 kcal/mol free energy as compared to 18. The HOMO of TS$_{18-19}$ corresponds to the interaction between the HOMO of 1 and the LUMO of C$_6$H$_5$. The LUMO of C$_6$H$_5$ receives electron density from HOMO of 1 (see Figure S5). The charges on the H atom and C atom near the Mg atoms are $-0.27$ and $-0.66$ lel, respectively, in TS$_{18-19}$ (see Table S2). There is no considerable change in the charge distribution of the rest of the benzene molecule ($q$(rest-C$_6$H$_5$) = $-0.04$ lel) as compared to that in the free C$_6$H$_5$. The total charge of C$_6$H$_5$ is $-0.97$ lel, which suggests the flow of electron density from 1 to C$_6$H$_5$.

The TS$_{18-19}$ is transformed to 19, which is 36 kcal/mol lower in free energy as compared to TS$_{18-19}$. The geometry of 19 is almost similar to that of 16. One H atom forms a bridge between the two Mg atoms, and the C$_6$H$_5$ unit is bound to only one Mg atom. After this point, the $\mu$-H starts to move inward, which gives TS$_{19-20}$ with a gain in 2.5 kcal/mol in free energy as compared to 19. Finally, the $\mu$-H went to the opposite side of the N4-plane, and the final complex Mg$_2$EP($\mu$-C$_6$H$_5$)($\mu$-H), 20, is formed; 20 has one bridging H atom and one bridging C$_6$H$_5$ group. The total free energy change for the whole process is $-22.1$ kcal/mol.

Smallest Mg–Mg Distance. Another important characteristic of 4, 17, and 20 is that these geometries correspond to the smallest Mg–Mg distance without having any bond between them. We have considered the Mg–Mg distances in some known bridged [Mg$_2$] complexes, viz., Mg$_2$H$_4$ (21), Mg$_2$F$_4$ (22), [(Nacnac)Mg($\mu$-H)$_2$]$_2$ (23), $^{70}$ [(DippNacnac)Mg($\mu$-H)$_2$]$_2$ (24), $^{82}$ [(DippNacnac)Mg($\mu$-H)($\mu$-1)Mg]$_2$ (25), and [(DippNacnac)Mg($\mu$-H)($\mu$-1)Mg]$_2$ (26).
respectively. Thus, Mg<sub>2</sub>EP is an excellent choice for the activation of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub> by Mg<sub>2</sub>EP are fairly high to be used for practical purposes. The current work provides us with a recipe toward a transition-metal-free catalytic process. Future modification of the ligand as well as the use of different metals might lower the activation barrier further and might be used as a better catalyst.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03006.

Representation of atomic numbers in 1 as used in the ADMP study, plots of the fluctuations of the Mg-N bonds in 1 against time, Mg−Mg natural bond orbital, plot of NCI isosurface, geometrical parameters for the small molecules, frontier molecular orbitals of the intermediates and TSs and the coordinates of the geometries (PDF)

ADMP simulations (AVI) (AVI)

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### SUMMARY AND CONCLUSIONS

The extended 3.1.3.1 [22]porphyrinoid system, H<sub>2</sub>EP, can stabilize the Mg<sup>2+</sup> ion. Gas-phase calculations within the DFT framework have shown that this bimetallic Mg<sub>2</sub>EP complex is thermochemically and kinetically stable. The complex possesses one Mg−Mg σ-bond, which is formed mainly by the 3s and 3p orbitals on the Mg atoms. The AIM analysis revealed the presence of an NNA near the midpoint of the two Mg atoms. The electron population at the NNA is high, and the $V^2\rho(r) < 0$ at NNA. An ELF basin has been identified with 61% localization. The computed average linear polarizability ($\alpha$), first hyperpolarizability ($\beta$), and second hyperpolarizability ($\gamma$) for Mg<sub>2</sub>EP are 493.7, 3.62 $\times$ 10<sup>5</sup>, and 1.1 $\times$ 10<sup>6</sup> au, respectively. Thus, Mg<sub>2</sub>EP can be used as a nonlinear optical material. The properties determined by the AIM and NLO analyses suggest that the Mg<sub>2</sub>EP can be considered as an organic electrode material. Furthermore, five small molecules, viz., H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub> are shown to get activated using Mg<sub>2</sub>EP. The H−H bond gets cleaved and finally forms a complex with two hydrido bridges. The inert aliphatic (CH<sub>4</sub>) and aromatic (C<sub>6</sub>H<sub>6</sub>) C−H bond activations can be achieved by the Mg<sub>2</sub>EP complex. Further, the activated C−H bond can be broken, and it may form one μ-H and one μ-CH<sub>3</sub> or μ-C<sub>6</sub>H<sub>6</sub> bonded complex. Thus, Mg<sub>2</sub>EP has the potential to be used as a catalyst for C−H bond activation. The global warming gases like CO<sub>2</sub> and N<sub>2</sub>O are effectively split to CO and N<sub>2</sub>, respectively. Thus, Mg<sub>2</sub>EP is an excellent choice for the activation of these pollutant gases. The free energy barriers for the activation of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub> by Mg<sub>2</sub>EP are fairly high to be used for practical purposes. The current work provides us with a recipe toward a transition-metal-free catalytic process. Future modification of the ligand as well as the use of different metals might lower the activation barrier further and might be used as a better catalyst.

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