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On the Stability of Noble Gas bound 1-Tris(pyrazolyl)borate Beryllium and Magnesium Complexes

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Abstract

An *in silico* study is performed to assess the noble gas (Ng) binding ability of 1tris(pyrazolyl)borate beryllium and magnesium cationic complexes (TpBe⁺ and TpMg⁺). The Be and Mg centers in these complexes are found to bind the heavier Ng atoms quite effectively. Both the zero point energy and basis set superposition error corrected dissociation energy values for the bonds between Ar-Rn and metal atoms range within 5.8-10.2 kcal/mol for Be and 5.2-9.9 kcal/mol for Mg. The dissociation of Kr-Rn bound analogues of TpBe⁺ and Ar-Rn bound analogues of TpMg⁺ into the individual Ng atoms and TpBe⁺ or TpMg⁺ complexes is endergonic in nature at room temperature. The remaining lighter Ng bound complexes would be stable at lower temperatures. The nature of Be-Ng or Mg-Ng bonds is explored via Wiberg bond indices computation, atoms-in-molecules and energy decomposition analyses. The degree of covalent character in the Be/Mg-Ng bonds increases gradually in moving from He to its heavier congeners. The Be-Xe/Rn and Mg-Xe/Rn bonds could be categorized as of partial covalent type. The contribution from the orbital term is the maximum towards the total attraction. The magnitude of this term becomes gradually larger from He to Rn implying larger degree of covalent character along the same.

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1. Introduction

The chemical inertness of noble gas (Ng) elements had always remained a subject of curiosity among chemists for a very long time. Earlier theoretical predictions^{1,2} were made regarding the viability of krypton and xenon fluorides based on which attempts to synthesize them did not give any success.³⁻⁵ In fact, attempts to synthesize any Ng compounds were not successful until 1962 when Bartlett⁶ first and followed by others⁷⁻⁹ reported the existence of the Ng compounds. It opened a new domain of chemistry having exciting prospects. Since then theoreticians¹⁰⁻¹⁵ and experimentalists¹⁶⁻²⁰ have been working in tandem to discover more such noble gas compounds. The utility of Ng compounds as potential source of fuel and oxidizers in reaction medium and their very wide application in the field of industry, medicine, agriculture make the search of new Ng compounds significant.²¹

It was found by *in silico* studies that quite high positive charge on a metal center enables it to polarize the electron density on Ng atoms enough to form a chemical bond.^{10a,22} Frenking and co-workers^{10a,10d} first demonstrated the Ng binding ability of BeO molecule due to the reasonably high positive charge on Be center. The interaction was found to be strong enough to stabilize NgBeO (Ng = Ar-Xe) compounds and consequently they were detected later via matrix infrared spectroscopy by Thompson and Andrews.^{18a} The short Ne-Be bond distance in NeBeS was found by Pyykkö²³ by the *ab initio* computation which was recently detected experimentally.²⁴ Thereafter, a series of NgBeY (Y = S, Se, Te, NH, NCN, NBO, CO_3 , SO_4) clusters is reported in the literature by different groups.²⁵⁻²⁷ The electron withdrawing ability of Y dictates the Ng binding ability of BeY. In fact, Grandinetti and co-workers^{14b,14e} further attempted to improve the Ng binding ability of BeO through interaction of it with a Lewis acid. Though He detachment energy in HeBeO-BH₃ became almost double than that of HeBeO, BeO-BH₃ is not of global minimum geometry rather HBeO-BH₂ is the corresponding lowest energy structure. Nevertheless, the conversion of BeO-BH₃ into HBeO-BH₂ is kinetically protected by almost 3 kcal/mol activation energy barrier.^{14e} Even, the stability of multiple Ar bound multicharged BeO (Ar_nBeO^{q+}) clusters was analyzed recently.²⁸ The variation of Ng binding ability of BeNH upon the substitution of -H group with different groups was also studied.^{25b} Even, a number of polynuclear complexes having -NBeHe moieties was proposed computationally.^{14c} BeN-CN and BeN-BO clusters were also reported recently having higher Ng

binding ability than those of BeO and BeNH.^{26b} Few other Ng bound Be containing clusters like Be_2N_2 , Be_3N_2 and $BeSiN_2$ were also found to be viable candidates.²⁹ Ghanty and co-workers^{15b,15c} further proposed metastable HBeNgF and FMNgF (M = Be, Mg; Ng = Ar-Xe) compounds having M-Ng chemical bonds.

On the other hand, there are only few studies on the noble gas compounds containing Mg-Ng bond. In 1973, Hayes et al.³⁰ noticed that the interaction of Ng with MgF₂ is strong enough to distort MgF₂ from its linear configuration. The bonding of M^+ and M^{2+} (M = Be, Mg) with Ng atoms was analyzed by Breckenridge and co-workers.³¹

1-tris(pyrazolyl)borate (Tp⁻) is an anionic tridentate and tripodal ligand, which is very well known for its coordination power with different metal atoms.³² Recently, Naglev et al.³³ synthesized and characterized a series of TpBeX (X = F, Cl, Br, I, H, D, N₃) complexes. A derivative of Tp₂Mg was also synthesized a few years back by Zagermann et al.³⁴ In this present study, we considered TpBe⁺ and TpMg⁺ complexes to explore their Ng binding ability. Dissociation energy and the thermochemical parameters like dissociation enthalpy and free energy change show that they are good candidates for binding Ng atoms, particularly Ar to Rn. TpBeNg⁺ and TpMgNg⁺ could be generated from TpBeF and TpMgF, respectively, by following the same techniques as those for the generation of NgSiF₃⁺ and NgSiF₂²⁺ from SiF₄ or XeGeF₃⁺ from GeF₄ or XeNF₂⁺ from NF₃.³⁵ The nature of interaction in forming the Be-Ng or Mg-Ng bonds is understood by Wiberg bond indices (WBI) computation,³⁶ atoms-in-molecules (AIM)³⁷ and energy decomposition analyses (EDA).³⁸

2. Computational details

The full optimization of all the studied clusters is carried out at the MPW1B95/def2-TZVP level.^{39,40} We have chosen MPW1B95 functional for the present study since in a benchmarking study on Ng compounds this functional was shown to well reproduce bond dissociation energy and bond distance similar to those at the CCSD(T) level.⁴¹ Harmonic vibrational frequencies are computed to characterize the nature of the stationary states and to make the zero point vibrational energy (ZPE) corrections. A quasi-relativistic pseudopotential is employed for core electrons of the Xe and Rn atoms.⁴² The correction to basis set superposition error (BSSE) is included through the standard counterpoise (CP) method proposed by Boys and Bernardi.⁴³ Natural population analysis (NPA) and the calculation of WBI³⁶ are carried out to evaluate the atomic charges (q) at each center and to assess the bond order, respectively. All these computations are performed by using Gaussian 09 program package.⁴⁴ The atoms-in-molecules (AIM) analysis³⁷ is carried out by using Multiwfn software⁴⁵ at the MPW1B95/def2-TZVP level. EDA³⁸ in conjunction with Natural Orbital for Chemical Valence (NOCV)⁴⁶ is performed at the revPBE-D3/TZ2P//MPW1B95/def2-TZVP⁴⁷ level using ADF(2013.01) program package.⁴⁸ The revPBE-D3 functional is considered as here Grimme and coworkers⁴⁹, in their benchmark study, argued that revPBE-D3 functional is one of the currently most robust GGA functionals for the related systems. Zeroth order regular approximation (ZORA)⁵⁰ is adopted to consider scalar relativistic effects for the heavier atoms.

3. Results and discussion

3.1. Structure and stability

The optimized geometries of TpMF and TpM^+ (M = Be, Mg) complexes are displayed in Figure 1.



Figure 1. The optimized geometries of TpMF and TpM⁺ (M = Be, Mg) at the MPW1B95/def2-TZVP level. The M-N and M-F bond lengths are given in Å unit within square brackets and the charges on M centers are provided in au within parentheses.

The minimum energy structures of TpBeF and TpMgF correspond to the C_{3v} point group with ¹A₁ electronic state. Loss of F⁻ generates TpM⁺ and the geometry maintains C_{3v} point group with one site of M center available for further coordination. Moreover, the M center carries large positive charge, being 1.27 |e| for Be and 1.61 |e| for Mg. Therefore, the large positive charge on M center indicates that the polarizing power of the same would be reasonably high to deform the electron density on Ng center, thereby allowing it to form a chemical bond. We found that TpM⁺ can indeed bind Ng atoms quite effectively having both ZPE and BSSE corrected dissociation energy (D₀^{BSSE}) values of 0.9, 1.7, 5.8, 7.6, 9.3 and 10.2 kcal/mol for the dissociation of He, Ne, Ar, Kr, Xe and Rn atoms, respectively, from TpBeNg⁺ (see Figure 2 and Table 1).



Figure 2. The optimized geometries of $TpMNg^+$ (M = Be, Mg; Ng = He-Rn) at the MPW1B95/def2-TZVP level. The M-Ng bond lengths are given in Å unit.

In case of TpMgNg⁺, the respective D_0^{BSSE} values are a little bit smaller than that of TpBeNg⁺, D_0^{BSSE} values being 0.2, 1.6, 5.2, 6.8, 8.8 and 9.9 kcal/mol for the dissociation of He,

Ne, Ar, Kr, Xe and Rn atoms from TpMgNg⁺, respectively (see Table 1). Note that although the positive charge on Mg center is higher than that on Be center, due to the larger radius of Mg (141 pm) than Be (96 pm) the polarizing power of the former is smaller than that of the latter. This is reflected from their D_0^{BSSE} values and the degree of electron transfer from Ng to cationic M center. NPA charge calculation reveals that the degree of electron transfer from Ng to Be center is larger than the corresponding electron transfer from Ng to Mg center. For Kr-Rn bound analogues almost 0.3 |e| is transferred from Ng to Be whereas in TpMgNg⁺, around 0.2 |e| is shifted from Kr-Rn to Mg center.

Table 1. ZPE and BSSE corrected dissociation energy $(D_0^{BSSE}, kcal/mol)$, dissociation enthalpy (Δ H, kcal/mol) and free energy change (Δ G, kcal/mol) at 298 K for the dissociation process: NgTpM⁺ \rightarrow Ng + TpM⁺, NPA Charge at M and Ng Centers (q, au), Wiberg bond indices of M–Ng Bonds (WBI), M–Ng bond distances (r_{M-Ng} , Å) and HOMO-LUMO energy gap (gap, eV) of TpMNg⁺ compounds computed at the MPW1B95/def2-TZVP level. (Ng = He-Rn; M = Be, Mg)

Complexes	D_0^{BSSE}	ΔH	ΔG	q_{Ng}	q_{M}	WBI	Gap	r _{M-Ng}
TpBe ⁺					1.27		6.22	
TpBeHe⁺	0.9	1.7	-4.8	0.10	1.12	0.19	7.06	1.743
TpBeNe ⁺	1.7	2.5	-4.5	0.07	1.18	0.13	7.06	2.019
TpBeAr ⁺	5.8	6.4	-0.9	0.19	1.07	0.33	7.07	2.258
TpBeKr ⁺	7.6	7.7	0.6	0.24	1.03	0.41	7.08	2.393
TpBeXe ⁺	9.3	9.4	3.2	0.30	0.97	0.51	7.08	2.567
TpBeRn ⁺	10.2	10.2	3.6	0.32	0.96	0.53	7.08	2.648
$TpMg^+$					1.61		5.38	
TpMgHe ⁺	0.2	1.0	-3.9	0.05	1.54	0.09	6.45	2.191
TpMgNe ⁺	1.6	2.0	-2.8	0.04	1.56	0.07	6.03	2.368
TpMgAr ⁺	5.2	5.4	1.1	0.11	1.48	0.20	6.45	2.591
TpMgKr ⁺	6.8	6.9	2.5	0.14	1.45	0.25	6.47	2.724
TpMgXe ⁺	8.8	8.7	3.3	0.18	1.40	0.32	6.42	2.913
$TpMgRn^+$	9.9	9.8	4.3	0.20	1.39	0.35	6.23	2.989

It may also be noted that the D_0^{BSSE} value gradually increases in moving from He to Rn following the periodic trend. This is due to the fact that with an increase in the size of the Ng atoms down the group, polarizability of Ng atom also increases. Hence, along the same, a positively charged M center can easily attract the electron cloud of Ng atom towards itself

facilitating the bond formation. All the dissociation processes are endothermic in nature and the endothermicity gradually increases down the group. The dissociation of TpMNg⁺ into TpM⁺ and Ng is accompanied by a favorable entropy term ($\Delta S = \text{positive}$) and unfavorable enthalpy term ($\Delta H = \text{positive}$). Therefore, at a particular temperature, the dissociation process would be thermochemically unfavorable in nature if ΔH term dominants over T ΔS term. In cases of Kr-Rn bound TpBe⁺ analogues and Ar-Rn bound TpMg⁺ analogues, the unfavorable ΔH terms are found to be large enough to make the dissociation process endergonic in nature is needed to be viable as favorable T ΔS term becomes less important at low temperature (see Table 1). In fact, we have computed ΔG values for the He and Ne analogues at 77 K and 4 K temperature (see Table 2). The corresponding ΔG values are turned out to be positive at these temperatures. In case of TpBeAr⁺, at slightly low temperature (250 K) the dissociation process becomes endergonic in nature.

Table 2. Free energy change (ΔG , kcal/mol) at 77 K and 4 K for the dissociation process: NgTpM⁺ \rightarrow Ng + TpM⁺ studied at the MPW1B95/def2-TZVP level.

Process	ΔG		
	At 4K	At 77K	
$TpBeHe^+ \rightarrow TpBe^+ + He$	1.2	0.3	
$TpBeNe \rightarrow TpBe^+ + Ne$	2.3	1.4	
$TpBeAr \rightarrow TpBe^+ + Ar$	6.3	4.6	
$TpMgHe \rightarrow TpMg^{+} + He$	0.9	-0.2	
$TpMgNe \rightarrow TpMg^{+} + Ne$	2.1	0.9	

High electronic stability of a system is reflected by a large gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. A large energy separation between HOMO and LUMO implies that neither it wants to accept an extra electron in the LUMO nor it is keen to leave an electron from HOMO. Consequently, the system could be treated as highly stable one. HOMO-LUMO energy gap is nothing but the hardness of the molecule. Therefore, the stability originated from the large HOMO-LUMO gap is related with the maximum hardness principle.⁵¹ In the present cases, the HOMO-LUMO energy gap is 6.22 eV for TpBe⁺ and 5.38 eV for TpMg⁺. In both cases, it is found to increase by almost 1.0 eV

in the Ng bound analogues compared to the unbound one (see Table 1). It indicates that Ng binding increases the electronic stability of the system.

The stretching frequencies of M-Ng bonds and their corresponding IR intensities are provided in Table S1 (supporting information). The M-Ng stretching frequency gradually decreases along He-Rn, being within the range of 317-73 cm⁻¹ for Be complexes and 241-61 cm⁻¹ for Mg complexes. The respective stretching modes exhibit very low IR intensities.

The valence orbital populations of M center as well as Ng center in the TpMNg⁺ complexes are provided in Table S2 (supporting information). The valence orbital populations of Be and Mg in TpBe⁺ and TpMg⁺ complexes are $2s^{0.26} 2p_x^{0.22} 2p_y^{0.22} 2p_z^{0.03}$ and $3s^{0.20} 3p_x^{0.08} 3p_y^{0.08} 3p_z^{0.02}$, respectively. The electron transfer mostly takes place from the p_z orbital of Ng atoms (1s orbital for He) to the vacant p_z orbital of M center. It may be noted that by symmetry M-Ng bond in TpMNg⁺ is placed along z direction. Therefore, the filled p_z orbital of Ng atom is more likely to interact with the co-aligned vacant p_z orbital of M center than the other p orbitals making such p_z-p_z interaction more favorable. Apart from the p_z orbital, the s orbital of Ng also participates to some extent in electron transfer.

Very small value of WBI is obtained for an M-He/Ne bond indicating a closed-shell type of interaction. However, it gradually improves in moving from Ar to Rn. In fact for Xe and Rn bound analogues of TpBe+, the WBI value is around 0.5 implying significant covalent character therein. On the other hand, the WBI values for the Mg-Ng bonds are somewhat smaller than those in the Be-Ng bonds. For Kr-Rn bound TpMg⁺ complexes, the WBI value is found to be around 0.3 (see Table 1).

It may be noted that though the D_0^{BSSE} value increases in moving from He to Ne, the degree of electron transfer from Ng to M and WBI of M-Ng bond somewhat decrease along the same. Based on the polarizability values, Ne should be more polarizable than He. As a result a greater degree of electron transfer should take place from Ne compared to He. But the reverse is true in the present cases. This observation is not exclusive only for the present systems, in our earlier studied Ng-Be systems^{26,29} as well as in the other systems reported in the literature⁵² similar trend was observed. In fact, in some cases the Ne compounds were found to be less stable with a lower bond dissociation energy than that of the He compounds.^{26b} This puzzling behavior

8

of Ne is well known. Grandinetti⁵³ described this fact nicely in his article entitled "Neon behind the signs".

3.2. Atoms-in-molecules analysis

Various topological descriptors at the bond critical points (BCPs) of M-Ng bonds obtained from the AIM analysis³⁷ are provided in Table 3. The electron density concentration and depletion at the BCP are indicated by the negative and positive values of Laplacian of electron density ($\nabla^2 \rho(r_c)$), respectively. The concentration and depletion of electron density in turn imply covalent and noncovalent interactions, respectively. However, many shortcomings of this descriptor were also reported.^{54,37pp.312-314} Some other descriptors like electron energy density (H(r_c)) and the ratio of local kinetic energy density (G(r_c)) and electron density ($\rho(r_c)$) were also introduced to describe a bond. It was argued that if H(r_c) < 0 or G(r_c)/ $\rho(r_c)$ < 1, then the bond might be considered as at least of partial covalent type.^{55,56}

Table 3. Electron density descriptors (au) at the bond critical points (BCP) of Ng-M bond in TpMNg⁺ obtained from the wave functions generated at the MPW1B95/def2-TZVP Level.

Complexes	$\rho(r_{\rm c})$	$\nabla^2 \rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$G(r_c)/\rho(r_c)$
TpBeHe ⁺	0.014	0.142	0.028	-0.021	0.007	2.033
TpBeNe ⁺	0.012	0.114	0.023	-0.018	0.005	1.938
TpBeAr ⁺	0.019	0.131	0.030	-0.026	0.003	1.542
TpBeKr ⁺	0.020	0.113	0.027	-0.026	0.001	1.352
TpBeXe ⁺	0.021	0.090	0.024	-0.026	-0.002	1.131
TpBeRn⁺	0.021	0.077	0.022	-0.025	-0.003	1.031
TpMgHe ⁺	0.008	0.056	0.010	-0.006	0.004	1.263
TpMgNe ⁺	0.009	0.068	0.013	-0.008	0.004	1.367
TpMgAr ⁺	0.015	0.083	0.017	-0.013	0.004	1.121
TpMgKr ⁺	0.016	0.073	0.016	-0.013	0.003	1.002
TpMgXe ⁺	0.016	0.057	0.013	-0.012	0.001	0.843
$TpMgRn^+$	0.016	0.051	0.012	-0.012	0.001	0.783

Both, in Be-Ng and Mg-Ng bonds, $\nabla^2 \rho(r_c)$ values are found to be positive. The contour plots of $\nabla^2 \rho(r)$ for TpBeNg⁺ and TpMgNg⁺ are displayed in Figures 3 and S1 (in supporting information), respectively.

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Figure 3. The plots of Laplacian of electron density $(\nabla^2 \rho(r))$ of TpBeNg⁺ complexes at the MPW1B95/def2-TZVP level.

For the lighter analogues, the shapes of the valence orbitals of Ng atoms undergo negligible changes implying almost noncovalent bonds. However, the deformation is reasonably large for Xe and Rn analogues indicating the presence of some degree of covalent character. Moreover, for Be-Xe and Be-Rn bonds, we found $H(r_c)$ values as negative which implies that they have the partial covalent character. But another descriptor, $G(r_c)/\rho(r_c)$ values are greater than 1 for these two bonds. Nevertheless, for Be-Xe/Rn bonds, the WBI value indicates that almost half a bond order occurs there. From these observations although $G(r_c)/\rho(r_c)$ is found to be greater than 1, these bonds are categorized as of partial covalent type. It is also worth noting that the failure of some of these descriptors in analyzing the nature of bond in many instances was already reported in literature.^{11a, 54,37pp.312-314} So this is not very surprising that $G(r_c)/\rho(r_c)$ gives unconvincing results. Proper caution needs to be taken for using these descriptors to explain the nature of a bond. On the other hand, both $\nabla^2 \rho(r_c)$ and $H(r_c)$ are found to be positive for all Mg-Ng bonds. However, $G(r_c)/\rho(r_c)$ values are less than 1 for Mg-Xe and Mg-Rn bonds implying them as of partial covalent type.

3.3. Energy decomposition analysis

We have performed EDA to get further insight into the bonding situation⁵⁷ by decomposing the total interaction energy (ΔE_{total}) into the Pauli repulsion (ΔE_{Pauli}), electrostatic (E_{elstat}), orbital (ΔE_{orb}) and dispersion (ΔE_{disp}) energy terms (see Table 4). In the fragmentation scheme, TpM⁺ and Ng are considered as two interacting fragments.

Complexes	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{disp}
TpBeHe ⁺	-1.4	6.5	-1.2(15.0)	-5.7(72.4)	-1.0(12.6)
TpBeNe ⁺	-2.0	6.9	-1.9(21.4)	-5.5(62.3)	-1.5(16.4)
TpBeAr ⁺	-7.3	13.1	-3.1(15.0)	-13.9(68.4)	-3.4(16.6)
TpBeKr ⁺	-9.8	14.6	-3.3(13.6)	-16.9(69.3)	-4.2(17.0)
TpBeXe ⁺	-12.9	16.4	-3.6(12.4)	-20.6(70.5)	-5.0(17.2)
TpBeRn ⁺	-14.3	17.0	-3.7(11.9)	-21.9(70.0)	-5.7(18.1)
TpMgHe ⁺	-1.4	2.0	-0.4(11.6)	-2.7(79.5)	-0.3(8.9)
TpMgNe ⁺	-2.3	2.6	-0.8(16.3)	-3.5(71.7)	-0.6(12.0)
$TpMgAr^+$	-5.9	6.2	-1.5(12.3)	-9.4(77.4)	-1.2(10.2)
TpMgKr ⁺	-8.1	7.3	-1.7(10.9)	-12.1(78.9)	-1.6(10.1)
TpMgXe ⁺	-10.6	8.1	-1.8(9.4)	-15.0(80.4)	-1.9(10.2)
$TpMgRn^+$	-11.7	8.6	-1.8(9.0)	-16.3(80.3)	-2.2(10.8)

Table 4. EDA results of the TpMNg⁺ complexes studied at the revPBE-D3/TZ2P//MPW1B95/def2-TZVP level. All the energy terms are in kcal/mol.

(The values within the parentheses are in percentage and show the contribution towards the total attractive interaction $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$)

The negative sign in an energy term implies attractive interaction whereas positive sign represents a repulsive one. In all cases, the contribution from the ΔE_{orb} term is found to be the maximum towards the total attraction ranging from 62-80%. For lighter Ng atoms, the ΔE_{elstat} term contributes slightly more than that of ΔE_{disp} term towards the total attraction. However, for the heavier Ng atoms, the reverse is true. The plot of deformation densities ($\Delta \rho$) of the pair-wise orbital interactions and the associated ΔE^{orb} energies obtained from the EDA-NOCV reveal that the electron cloud shifted from the Ng center is accumulated in between the M and Ng centers (see Figure 4 for Be complexes and Figure S2 in supporting information for Mg complexes). According to the present color code, electron charge flew from red to blue. The ΔE^{orb} energies associated with these interactions gradually increase in moving Ar to Rn. Since the ΔE_{orb} term accounts for charge transfer and polarization, a large ΔE_{orb} value in a bond implies the presence of significant covalent character therein. In our cases, in moving from Ar to Rn the magnitude of ΔE_{orb} value gradually increases implying an increased covalent character along the same. It may be noted that for a given TpMNg⁺ the contribution of ΔE_{orb} term is larger in Be analogue than that in Mg analogue. It signifies that the degree of covalent character is somewhat larger in a Be-Ng bond than that in an Mg-Ng bond. The lower WBI values in the Mg-Ng bonds than that in the respective Be-Ng bonds also confirm this fact.



Figure 4. The plot of deformation densities ($\Delta \rho$) of the pair-wise orbital interactions and the associated ΔE^{orb} energies obtained from the EDA-NOCV. ΔE^{orb} values are given within the parentheses in kcal/mol.

4. Conclusions

Owing to large positive charge on M center, $TpBe^+$ and $TpMg^+$ are able to bind Ng atoms effectively, particularly from Ar to Rn atoms. The ZPE and BSSE corrected dissociation energy value for the Be-Ng bond in $TpBeNg^+$ ranges from 0.9 to 10.2 kcal/mol whereas it is somewhat smaller for the Mg-Ng bond in $TpMgNg^+$ in which it ranges from 0.2 to 9.9 kcal/mol with gradual increase in moving from He to Rn. In $TpBeNg^+$, almost 0.3 |e| and 0.2 |e| are transferred from Kr-Rn to Be and Mg centers, respectively. The electron transfer occurs mostly from the p_z

orbital of Ng atoms (1s orbital for He) to the vacant p_z orbital of M center. The dissociations of Kr-Rn bound TpBe⁺ and Ar-Rn bound TpMg⁺ complexes into individual Ng atoms and TpM⁺ are found to be endergonic in nature at room temperature. However, the lighter Ng bound TpM⁺ analogues are viable at lower temperature. In the Ng bound analogues, the HOMO-LUMO gap improves by almost 1.0 eV compared to that in the unbound one. It implies an increased electronic stability upon Ng binding. The values of Wiberg bond indices corresponding to the M-Ng bonds gradually increase along Ar-Rn. Almost half a bond order is found for Be-Xe/Rn bonds. The computation of various topological descriptors reveals that the M-Xe/Rn bond could be called as of partial covalent type. The orbital energy term is found to be the maximum contributor towards the total attraction. The magnitude of orbital energy term in the M-Ng bonds increases gradually in moving from He to Rn, signifying a larger degree of covalent character along the same. For a given Ng, Mg-Ng bond is found to be somewhat less covalent in nature than the corresponding Be-Ng bond.

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1-tris(pyrazolyl)borate beryllium and magnesium cationic complexes are found to bind Ar-Rn atoms quite effectively.