



Neutral all metal aromatic half-sandwich complexes between alkaline earth and transition metals: an ab initio exploration

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Abstract

Sandwich complexes find their interests among the chemists after the breakthrough discovery of ferrocene. Since then, a number of sandwich and half-sandwich complexes were predicted and synthesized. Herein, we have theoretically proposed a series of half-sandwich complexes involving a neutral Be₃ ring and transition metal. Quantum chemical calculations have shown that the proposed complexes are quite stable involving high bond dissociation energies. The thermodynamics of their formation is also favorable. The Be₃ ring in all cases possesses dual aromaticity which has been ascertained based on magnetic as well as topological feature of electron density.

Keywords Half-sandwich complexes · Dual aromaticity · Topological analyses

Introduction

Discovery of the first sandwich complex (C₅H₅)₂Fe, commonly known as “ferrocene,” drew the attention of the chemistry fraternity in no time [1–3]. The detail structural analyses revealed that the complex may adopt two close energy conformations [4]. This was followed by the discovery of sandwich complexes involving benzene and other arene systems coordinated to transition metals via delocalized π -electrons [5]. Since then, the journey of this domain has been spectacular as numerous sandwich complexes were proposed and synthesized along and their bonding analyses were carried out [6–34]. As compared to that of a full sandwich complex where the metal center

is enclosed on both sides, half-sandwich metallocenes involve a metal atom or ion enclosed on one particular side only. The inception of half-sandwich complex took place almost parallel to the discovery of ferrocene when Fischer and Hafner carried out the synthesis of tetracarbonyl (cyclopentadienyl) vanadium complex, C₅H₅V(CO)₄ [35]. This was followed by the synthesis of half-sandwich compounds containing manganese and cobalt as metal centers [26–37]. Recently, Pan et al. synthesized all metal aromatic sandwich compound [Sb₃Au₃Sb₃]^{3−} where Au₃ ring is sandwiched by two cyclo-Sb₃ rings [38]. It is worth mentioning here that previously such all metal sandwich complexes have been predicted theoretically [39–46].

Although all metal sandwich complexes have so far been significantly explored, the library of such complexes involving *s*-block metal as ligand fragment is not adequate so far [47, 48]. Through this ab initio study, we have designed a series of all metal neutral half-sandwich complexes (Scheme 1) involving Be₃ fragment attached to transition metals. The reason of taking cyclic Be₃ fragment is due to the fact that it can act like a Z-type ligand owing to the presence of vacant π symmetric orbital. The structure and reactivity of Be₃ is well established [49–51]. The proposed half-sandwich complexes feature donor-acceptor interaction between the transition metals and the Be₃ fragment. These complexes are quite stable owing to their high bond dissociation energies and also with favorable thermodynamics.

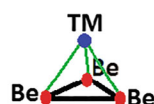
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TM = Fe, Ru, Os, Zn, Cd, Hg

Scheme 1 Half-sandwich complexes of Be₃ fragment with transition metals

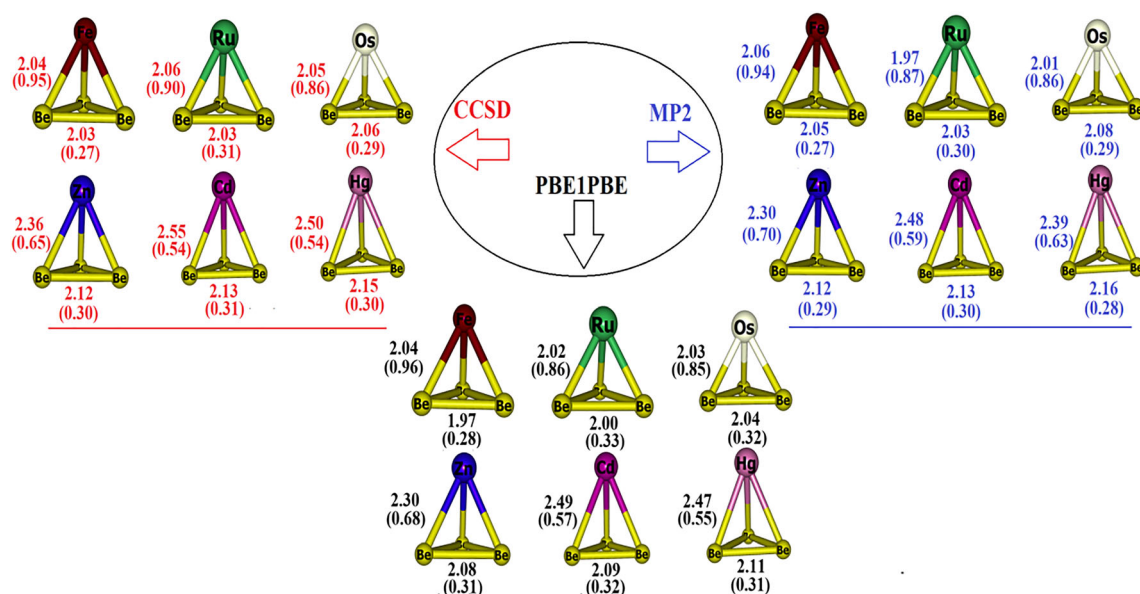


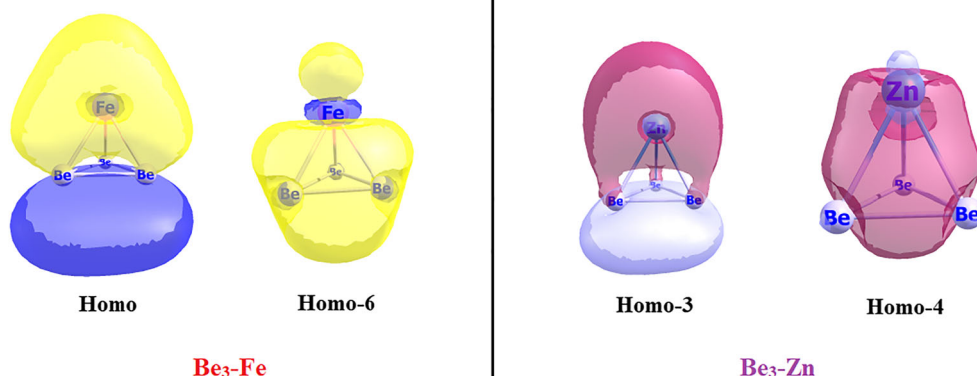
Fig 1 Optimized geometries of the molecules at different theory levels considered. Bond lengths are in Å. Wiberg bond indices are given in parenthesis

Computational details

All the molecules were fully optimized without any symmetry constraints in their gas phase at PBE1PBE [52], MP2 [53], and CCSD level of theory using 6-311++G** basis set for Be atom and SDD [54] basis set for transition metals. Harmonic frequency calculations were performed at the same level of theory to characterize the nature of stationary states. The global minima structures have all real values of frequencies. All energies

are zero point and thermal corrected. Natural bond orbital analyses (NBO) [55] were performed at the above mentioned theory levels to get the precise idea of the frontier orbitals as well as electronic structure of the molecules. All calculations were performed using Gaussian 16 suite of program [56]. Quantum theory of atoms in molecules (QTAIM) [57, 58] electron localization function (ELF) [59, 60], and charge decomposition analysis (CDA) [61] were performed at PBE1PBE level of theory using Multiwfn program code [62].

Fig 2 Frontier Kohn-Sham orbitals of Be₃-Fe and Be₃-Zn system

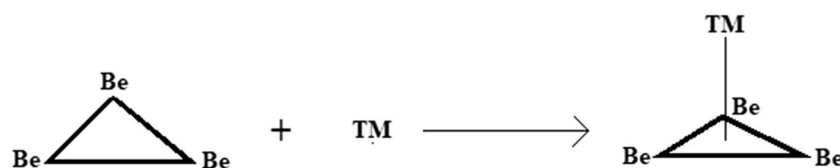


Results and discussion

Figure 1 shows the optimized geometries of the molecules at CCSD, MP2, and PBE1PBE theory levels. All these molecules are closed shell singlet in their global minima with C_{3v} symmetry. The relative energies of different possible isomers are listed in Table S1, supporting information. Among the studied systems, the frontier molecular orbitals of the Be_3 –Fe and Be_3 –Zn have been shown (Fig. 2). The Be–Be distance in metal free cyclic Be_3 molecule is 2.210 Å which significantly shortens in the half-sandwich complexes (Fig. 1). The Wiberg bond indices for the TM–Be bonds, a measure of bond strength, are found to be higher for Fe, Ru, and Os complexes than those of in Zn, Cd, and Hg complexes (Fig. 1).

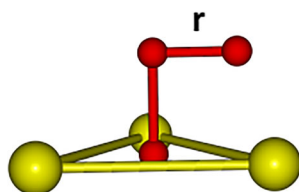
To investigate the mode of binding of Be_3 fragment with the transition metals, we calculated the energy changes while displacing the transition metal atom from the center to a distance r as shown in Scheme 2. Results based on single-point calculations at PBE1PBE level of theory (Fig 3) reveal that all

We then turned to the aromaticity of the proposed molecules by performing nucleus-independent chemical shift (NICS) calculations at the center of the Be_3 fragment in the complexes which is known as NICS(0) and 1 Å above the plane which we designated as NICS(1) [61] (Scheme 3, Table 1). It is worth mentioning that Be_3 ring is anti-aromatic which is backed by positive NICS(0) value of 20 ppm. Upon complexation with the considered transition metals, significant aromaticity is induced in the Be_3 –TM complexes. In all the complexes, aromaticity is dominated by NICS(0), a measure of σ aromaticity. However, NICS(1) values, a measure of π aromaticity, are also significant. Thus, the calculated values of NICS suggest that the proposed sandwich complexes have dual σ and π aromaticity [63]. The presence of dual aromaticity is expected to increase the stability of the complexes. We therefore, calculated the bond dissociation energies (BDE, Table 2) and change in Gibbs free energies (ΔG_{298}) of their formation according to the following equation:



these complexes have the lowest energy at $r = 0$, i.e., Be_3 fragment in these complexes feature η^3 coordination mode.

Further, to investigate the nature of bonding, we have performed charge decomposition analysis (CDA) Fe and Zn complexes respectively as representative case. Figure 4 shows the interaction diagram. The LUMO (lowest unoccupied molecular orbital) and LUMO+1 of Be_3 fragment interact with the metal d_z^2 and s orbital. It is to be noted that the LUMO of Be_3 fragment is a delocalized unoccupied π symmetric orbital while the LUMO+1 is the σ orbital. Occupation of these orbitals in the sandwich complex is expected to enhance aromaticity in the cyclic Be_3 fragment.



Scheme 2 Displacement (r) of the transition metal atom parallel to the Be_3 plane

The BDE values were calculated by considering the neutral Be_3 and transition metal fragment. It is evident from Table 2 that all these complexes have high bond strength. The calculated BDE values are higher for Fe, Ru, and Os while they are lower for Zn, Cd, and Hg. The calculated values of the force constant (k , Table 2) are also higher for Fe, Ru, and Os. Moreover, the change in Gibbs free energies (ΔG_{298}) for their formation is more negative for Fe, Ru, and Os. However, ΔG_{298} values are negative in all cases suggesting their favorable thermodynamics of formation.

We then further analyzed the topological feature of electron density within the realm of quantum theory of atoms in molecules (QTAIM) [57, 58] and electron localization function (ELF) [59, 60]. QTAIM is based on topological properties of electron density and its derivatives. It describes the concept of bonding with the help of bond paths and critical points. The electron density (q) exhibits a maximum, a minimum, or a saddle point in space. These points are referred to as critical points (CPs). At this point, the first derivatives of $q(\text{rc})$ vanishes. The Laplacian ($\nabla^2\rho$) plays a very vital role in the characterization of chemical bonding. Generally, for covalent

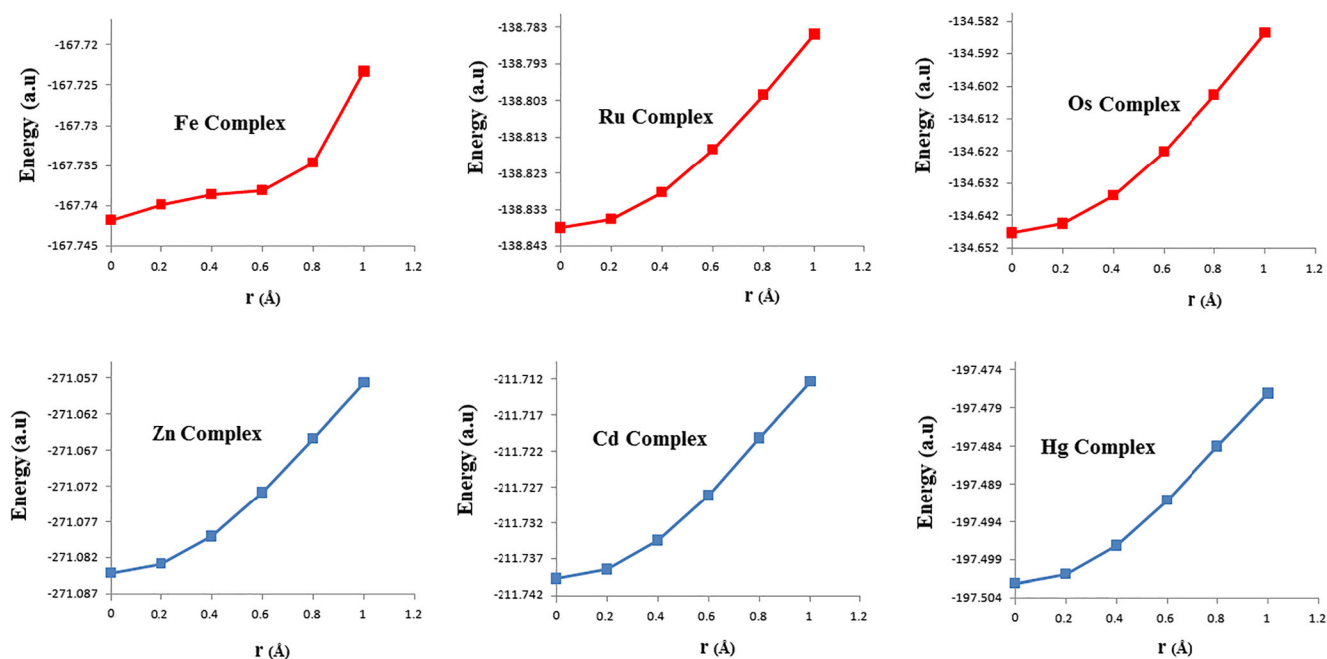


Fig 3 Plot of energy against the displacement (r) of the transition metal center in the sandwich complexes

Fig 4 Orbital interaction diagram of $\text{Be}_3\text{--Fe}$ and $\text{Be}_3\text{--Zn}$ complexes

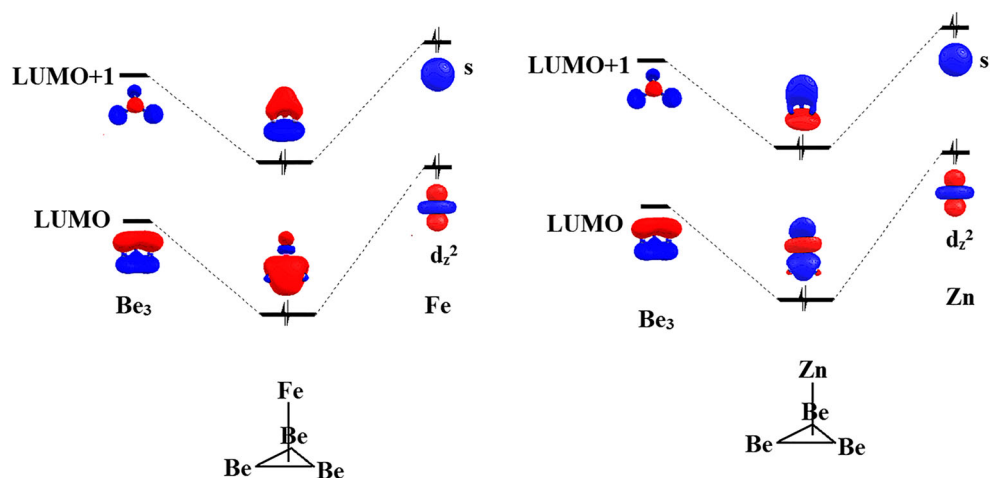


Table 1 PBE1PBE calculated NICS values (ppm) of the proposed half-sandwich complexes

Complexes	NICS (0) (ppm)	NICS (1) (ppm)
$\text{Be}_3\text{--Fe}$	−31.57	−4.33
$\text{Be}_3\text{--Ru}$	−25.45	−7.71
$\text{Be}_3\text{--Os}$	−34.53	−11.4
$\text{Be}_3\text{--Zn}$	−38.38	−15.72
$\text{Be}_3\text{--Cd}$	−35.48	−14.15
$\text{Be}_3\text{--Hg}$	−32.45	−12.81

interactions (also referred to as “open-shell” or “sharing” interactions), the electron density at the bond critical point (BCP), ρ_b , is large (>0.2 a.u.) while its laplacian, $\nabla^2\rho$, is large and negative. On the other hand, for closed-shell interactions (e.g., ionic, van der Waals, or hydrogen bonds), ρ_b is small (<0.10 a.u.) and $\nabla^2\rho$ is positive. However, a clear distinction between the closed-shell and covalent type of interaction is impossible without determination of the local electronic energy density, $H(r)$. The local electronic energy density, $H(r)$, given by $H(r) = G(r) + V(r)$, where $G(r)$ and $V(r)$ are the local kinetic and potential energy densities, is negative for an interaction with significant covalent character and accounts for the

Table 2 Bond dissociation energies (BDE, kcal/mol), ΔG_{298} (kcal/mol) of formation of proposed sandwich complexes and force constant, k (mDyne/Å)

Complex	BDE	ΔG_{298}	k
Be ₃ –Fe	96.17	–88.14	1.278
Be ₃ –Ru	154.86	–146.71	1.546
Be ₃ –Os	187.83	–179.65	1.323
Be ₃ –Zn	37.33	–29.67	0.62
Be ₃ –Cd	32.56	–25.05	0.43
Be ₃ –Hg	24.70	–17.25	0.32

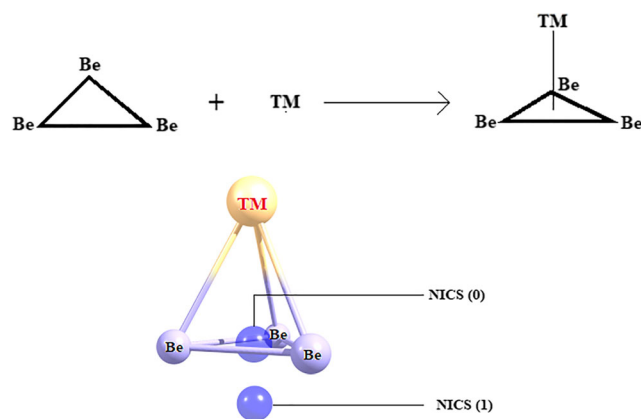
lowering of potential energy of electrons at BCPs. The magnitude of $H(r)$ reflects the “degree of covalency” present in a given interaction. Thus, some covalent (some polar bonds, donor–acceptor bonds, etc.) bonds are associated with positive values of $r_2 q$ and negative values of $H(r)$ [64]. Table 3 contains the numerical data at different bond critical points. The Be–TM bonds are characterized by positive values of laplacian, $\nabla^2\rho$, and negative values of local electronic energy density, $H(r)$, suggesting polar covalent character of these bonds [64]. The presence of significant amount of electron density at the Be–Be–Be ring critical points is an indication of aromaticity [57].

Conclusion

In conclusion, quantum chemical calculations were carried out to investigate the possibility of formation of Be₃–TM (TM = Fe, Ru, Os, Zn, Cd, Hg) half-sandwich complexes where the Be₃ fragment is acting as Z-type ligand. The stability of the proposed complexes is predicted by calculating BDE as well as the thermodynamic feasibility factor ΔG_{298} . The BDE values are found to be higher for Fe, Ru, and Os complexes

Table 3 Electron density, ρ , at the bond critical point (bcp) and ring critical points (rcp), laplacian of electron density, $\nabla^2\rho$, local electronic energy density, $H(r)$, and electron localization function, ELF, values. All values are in a. u.

Molecule	bcp/rcp	ρ	$\nabla^2\rho$	$H(r)$	ELF
Be ₃ –Fe	Be–Fe bcp	0.058	0.077	–0.028	0.22
	Be–Be–Be rcp	0.043	0.044	–0.006	0.43
Be ₃ –Ru	Be–Ru bcp	0.073	0.068	–0.035	0.18
	Be–Be–Be rcp	0.041	0.041	–0.005	0.45
Be ₃ –Os	Be–Os bcp	0.076	0.070	–0.035	0.16
	Be–Be–Be rcp	0.038	0.036	–0.007	0.48
Be ₃ –Zn	Be–Zn bcp	0.067	0.068	–0.032	0.18
	Be–Be–Be rcp	0.041	0.042	–0.008	0.34
Be ₃ –Cd	Be–Cd bcp	0.071	0.062	–0.033	0.16
	Be–Be–Be rcp	0.032	0.040	–0.005	0.28
Be ₃ –Hg	Be–Hg bcp	0.061	0.057	–0.031	0.14
	Be–Be–Be rcp	0.034	0.044	–0.005	0.28

**Scheme 3** Schematic representation of NICS values

compared to the Zn, Cd, and Hg complexes. However, the BDE values for the latter complexes are also significant enough for their realization. The calculated ΔG_{298} values are found to be significantly negative for all the geometries. Nucleus-independent chemical shift (NICS) calculations suggest the presence of dual aromatic character in the cyclic Be₃ fragment of the complexes which were substantiated by topological analyses. We feel that our ab initio study will attribute to the possible synthesis and characterization of the proposed complexes.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11224-021-01807-w>.

Availability of data and material The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Code availability Not applicable

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Declarations

Conflict of interest The authors declare no competing interests.

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