Coordination diversity of the phenazine ligand in binuclear transition metal sandwich complexes: Theoretical investigation

Meriem Merzoug [a], Bachir Zouchoune [a, b, *]

[a] Laboratoire de Chimie appliquée et Technologie des Matériaux, Université Larbi Ben M'Hidi-Oum el Bouaghi, 04000 Oum el Bouaghi, Algeria
[b] Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, Université-Constantine 1 (ex Mentouri-Constantine), Algeria

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ABSTRACT

DFT calculations with full geometry optimization have been carried out for all the low-energy isomers of $[M(C_{12}N_2H_8)]_2$ (M = Sc−Ni and $C_{12}N_2H_8$ = phenazine ligand = Phz). Depending on the metal atoms, phenazine adopts various hapticities that involve full or partial coordination of the C_6 and C_4N_2 rings. Phenazine is also shown to be quite flexible with respect to the spin ground state. The phenazine ligand can be bound to the metals involving its C_6 and C_4N_2 rings or its outer C_6 ones through various coordination modes such as $\eta^4-\eta^4$, $\eta^6-\eta^4$ and $\eta^6-\eta^6$, giving rise to the conformations of types (**a**) and (**b**). This study has shown that the electronic communication between the metal centers depends on their oxidation state in harmony with the neutral, monoanionic and dianionic phenazine forms. The major structures showed the preference of the coordination in separate way of the metal centers apart from the Ti, V and Co ones. The MO plots, WBIs (Weber bond indices) obtained from the Weinhold nature bond order analysis and the metal−metal bond lengths gave a deeper insight on the metal−metal bonding. Energy decomposition analysis showed that the interactions in the studied compounds are governed by half covalent and half electrostatic character.

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Introduction

The discovery of the ferrocene in 1951 [1], has given rise to wide investigations of more metallocenes with various transition metals [2,3]. Nevertheless, the major part of these investigations has turned around the sandwich and half-sandwich mononuclear complexes containing transitional metals coordinating diverse ligands [4−24]. To the best of our knowledge, the studies about dimetallocene are less investigated. Thus, it is surprising to note the scarcity of polymetallic sandwich compounds in which several metals are sandwiched between two fused polycyclic or hetero-polycyclic systems. The pioneering work of Kaltz and co-workers has highlighted the first examples of iron binuclear sandwich compound Fe₂(as-indacene)₂ in 1964 [25], followed hereafter by the isolation of the bis(pentalene) nickel and cobalt complexes [26]. Since, an important number of binuclear sandwich compounds of various monocyclic (cot) [27,28] or polycyclic (pentalene, indenyl

and fulvalene) ligands have been isolated [29−37]. Recently, another sandwich compound has been synthesized and characterized, where two cobalt atoms are encapsulated into a rigid cage of two indenyl ligands [38]. However, Murahashi et al. have extensively investigated the polypalladium sandwich complexes in the last decade [39−42]. In this regard, we were, thus, encouraged to explore the field involving hetero-polycyclic ligands such as phenazine. On the basis of the success of previous experimental [43−48] and theoretical studies [49] of the transition metal π-bonded complexes involving carbon and nitrogen atoms, we were interested in the development of the phenazine ligand's coordination chemistry of binuclear sandwich complexes. The free phenazine molecule is an aromatic electron donating system (14 π-electrons), which is structurally related to and isoelectronic with acridine and anthracene presenting a delocalized scheme in accordance with a formal bond order of 1.5 [43]. Assuming that a binuclear complexation occurs either at the two C_6 rings or at C_6 and C_4N_2 rings, it appears from Scheme 1, that the phenazine can provide only a maximum of 10 or 12 π-electrons among 14 to the metal centers.

Phenazine is among the organic molecules that possess large and delocalized π systems capable of embarking in a significant charge transfer interaction with a transition metal, which is

* Corresponding author. Laboratoire de Chimie appliquée et Technologie des Matériaux, Université Larbi Ben M'Hidi-Oum el Bouaghi, 04000 Oum el Bouaghi, Algeria. Tel.: +213 6 62038183; fax: +213 32 423983.
E-mail addresses: b.zouchoune@univ-oeb.dz, bzouchoune@gmail.com (B. Zouchoune).
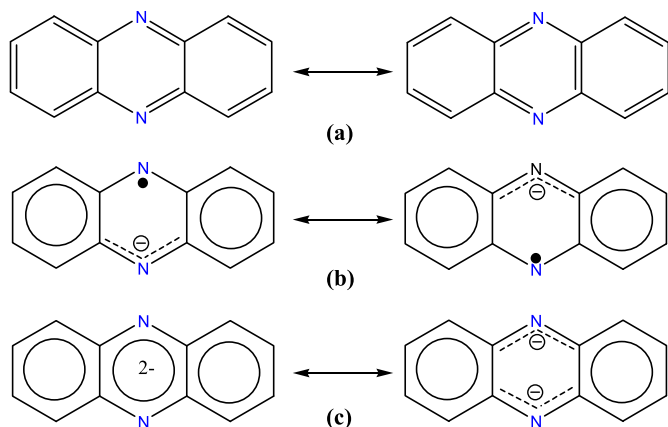
Scheme 1. Lewis representation of neutral (a), monoanionic (b) and dianionic (c) forms of the phenazine ligand.

particularly versatile, since it may act both as a regular neutral donor and a reduced ligand acting as mono- or dianion species, whose Lewis formula are shown in Scheme 1, engaging in electron transfer reactions with a wide variety of elements. Thus, it is involved in many electron transfers due to its easy reducible nature and can form complexes with transition metals [44]. In fact, the most attractive feature of these molecules as ligands is their aptitude to act as electron reservoir and to transfer spin density on require to and from the metal center. The main purpose of this work is the studying by means of DFT method the predicted low-lying states obtained by the interactions between the two phenazine rings in their various forms and the transition metals of the first row (Sc–Ni) in their different spin states. The metal–metal bonding is analyzed by using the molecular orbital plots and NBO method based on the WBIs (Wiberg bond indices).

Molecular structures

Depending simultaneously on the metal center positions and on the two phenazine ligands disposition, three structures are possible of the complexes of general formula [M(Phz)]$_2$ (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Phz = Phenazine), such as shown in Scheme 2. When
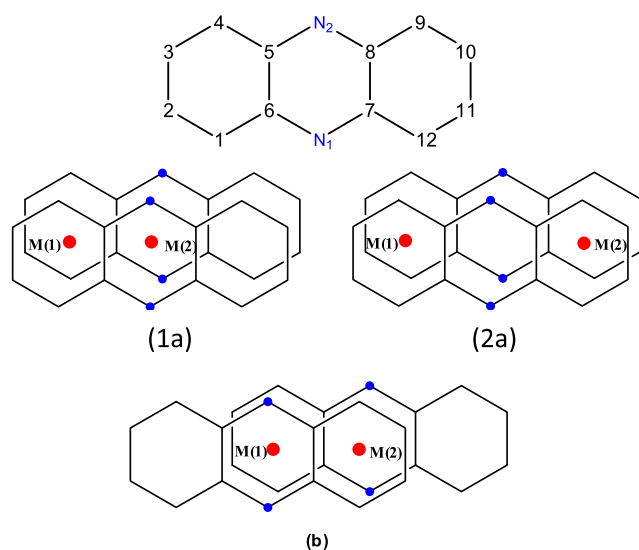
Scheme 2. Atom labeling used throughout this paper and the projected [M(Phz)]$_2$ structures of conformations (**1a**), (**2a**) and (**b**).

both phenazine ligands are totally eclipsed, one metal center can be coordinated to one C$_6$ ring of each phenazine, while the second metal can coordinate either C$_4$N$_2$ ring of each phenazine (conformation of type (**1a**)) or the remaining C$_6$ ring of each phenazine (conformation of type (**2a**)). The third possibility corresponds to the coordination to the neighboring C$_6$ and C$_4$N$_2$ rings in a partially eclipsed arrangement (conformation of type (**b**)). The (**1a**) and (**b**) conformations offer the possibility of direct metal–metal bonding. The geometries of the complexes [M(Phz)]$_2$ were optimized in their lowest states. The computed data are gathered in Tables 1 and 2 and selected optimized molecular structures are shown in Figs. 1, 3–9.

Results and discussion

[Sc(Phz)]$_2$ complexes

The [Sc(Phz)]$_2$ species are the less rich in electrons of the first row transition metals [M(Phz)]$_2$ series. For all conformations, the π-electrons of the coordinated rings are shared equitably by the two metals in conformity with the short Sc–C and Sc–N bond distances such as shown in Fig. 1 and in Supplementary information. Surprisingly, the singlet spin state [Sc(η^6,η^6-Phz)]$_2$ (**2a**), structure with C_s symmetry where both scandium metals are coordinated to the terminal C$_6$ rings of each phenazine is calculated as the most stable isomer. For such coordination mode, one phenazine ligand can be described as dianionic, but the second is considered as neutral, giving rise to monovalent Sc(I) metals. This global minimum structure displays strong Sc–C interactions, where the distances range from 2.443 to 2.572 Å giving an average 2.507 Å (See Supplementary information). These bond distances are in accordance with a perfect η^6 coordination mode of each coordinated ring, matching well with the neglected slippage of 9%. A small HOMO–LUMO gap of 0.34 eV is computed for this structure. The triplet spin state of the same conformation (**b**) is obtained less stable than the global minimum by 17.2 kcal/mol. For the latter isomer each of the two unpaired electrons is located on one metal center, showing a disfavored paramagnetic behavior than the diamagnetic.

Usually, the deficient structures tend to form metal–metal bonds in order to gain more stability and compensate the metallic need in electrons. However, it is not the case for the [Sc(η^6,η^6-Phz)]$_2$ (**1a**) singlet spin state structure with C_{2v} symmetry, which is expected to present triple metal–metal bond to reach a 16-MVE configuration for each Sc center. The Sc–Sc bond length of 3.225 Å, the MO plots (σ metal–metal bonding is occupied, but where π, δ, π*, δ* and σ* are vacant) and WBI of 0.18 (Wiber Bond Index), which is determined by Natural Bond Orbital (NBO) analysis [50] (with NBO 5.0 program) [51] show the presence of only a single bond following the electronic configuration: $(\sigma)^2(\pi)(\delta)^0$ $(\sigma^*)^0(\pi^*)^0(\delta^*)^0$. The structure's distortion is accompanied by a relative instability witnessed by an important folding angles of 30° (C(6)N(1)N(2)C(8) and C(6′)N(1′)N(2′)C(8′) dihedral angles). This distorted arrangement is due to strong π-π repulsions between the uncoordinated C$_6$ rings of the two phenazine ligands evidenced by the long distance $d_{Rcent\ldots R'cent}$ = 5.130 Å (Rcent = center of the C$_6$ ring), which disfavors the face-to-face arrangement. These π-π repulsions are well shown in Fig. 2(1), where 21a$_2$ and 29b$_2$ orbitals highlight clearly the antibonding character between the uncoordinated C$_6$ rings. The Sc–Sc bond length of 3.225 Å corresponds to a single bond, in agreement with the calculated NBO of and the MOs localization showing only σ Sc–Sc bonding orbital (38a$_1$). Therefore, the weak M–M bonding is associated with small HOMO–LUMO gap of 0.73 eV. The triplet spin state structure of the same conformation (**1a**) lies 6.3 kcal/mol above the corresponding spin state and 17.7 kcal/mol higher than the global minimum, but