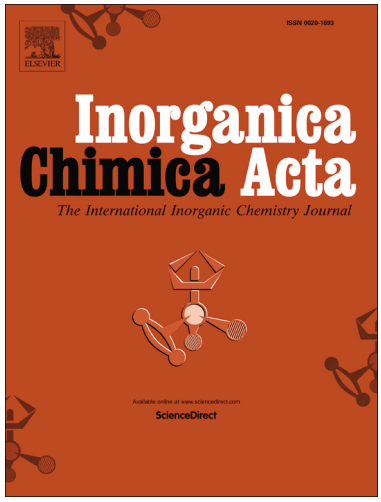

Research paper

Ligands' σ-Donation and π-Backdonation Effects on Metal-Metal Bonding in Trinuclear $[M_3(Tr)_2(L)_3]^{2+}$ (M = Fe, Ni, Pd, Pt, Tr = Tropylium and L = CO, HCN and C_2H_4) Sandwich Compounds: Theoretical Investigation

Bachir Zouchoune, Amira Saiad

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Bachir Zouchoune,[1,2*] Amira Saiad[1]

[1]Laboratoire de Chimie appliquée et Technologie des Matériaux, Université Larbi Ben M'Hidi- Oum El Bouaghi, (04000) Oum El Bouaghi, Algeria.

[2]Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, Université Constantine (Mentouri), (25000) Constantine, Algeria.

E-mail: b.zouchoune@univ-oeb.dz, Phone: +213 6 62038183, Fax: +213 32 423983

Abstract

DFT calculations with full geometry optimization using GGA BP86 and meta-GGA M06L functionals have been performed on the $[M_3(Tr)_2L_3]^{2+}$ (M = Fe, Ni, Pd, Pt, $Tr^+ = C_7H_7^+$ and L = CO, HCN and η^2-C_2H_4) sandwich complexes. The M_3 triangular core is encapsulated between two tropylium cations which tends to establish M-L bonding with regards to the metal nature and the spin state. It turned out that each tropylium cation is connected to the M_3 triangular core through an η^2,η^2,η^2 coordination mode engaging six carbon atoms amongst seven. For the Fe singlet structures, the calculated HOMO-LUMO gaps by both BP86 and M06L are small, thus favouring the triplet one. The $[Fe_3(Tr)L_3]^{2+}$ singlet structures are predicted to have two formal Fe-Fe single bonds and one formal Fe-Fe triple one within the Fe_3 triangle based on the bond distances and the Wiberg bond indices (WBIs), while their analogues of triplet state exhibit two formal Fe-Fe single bonds and one formal Fe-Fe double bond. For the nickel, palladium and platinum d^{10} metal structures, they display large HOMO-LUMO gaps and adopt three formal metal–metal single bonds within the M_3 core, in accordance with the small WBIs. The different binding capabilities of the isoelectronic CO, HCN and C_2H_4 auxiliary ligands are highlighted by the corresponding MOs' diagrams and their donation and backdonation amounts.

Key words:

Coordination chemistry, Electronic structure, NBO analysis, Bonding analysis.

***Corresponding author**