

The bond order concept applied to metal-metal interactions in binuclear complexes of the first row metals scandium to zinc: A DFT exploration

Fitzerald Hujon, Derek R. Langstieh and R. H. Duncan Lyngdoh

Department of Chemistry, North-Eastern Hill University, Shillong 793022, India

Binuclear lantern-type complexes are experimentally known for many transition metals. Metal-metal (MM) bonds in such complexes span a wide range of lengths, with MM bond orders of zero to five assigned to them. This DFT study uses the B3LYP and M06-L functionals with the cc-pVTZ basis set to treat binuclear lantern-type complexes of all the first row (3d) metals (Sc to Zn) using the formamidinate ligand. Firstly, the ground state spin multiplicities are predicted from considering various low-lying spin states. The DFT-derived spin multiplicities and MM bond lengths in the ground state complexes are compared with available experimental results. Formal bond order values are assigned to the MM interactions in all the ground state complexes on the basis of (a) occupancy of bonding and antibonding MOs, and (b) a novel electron counting method based on qualitative VB theory. Short MM bonds of higher bond order (3 to 5) are found in complexes of vanadium, chromium and manganese, while longer MM bonds of lower order (0 to 2) are found in complexes of scandium, titanium, iron, cobalt, nickel, copper, and zinc. Our DFT results generally predict MM bond lengths shorter than experiment.