

ABSTRACT

The research work presented in this thesis shows that suitable ligands can form stable complexes with the main group elements and group 12 metal atoms involving unusual bonding patterns. Sophisticated computational methods have been employed to optimize the geometries and to study the nature of the bonding in these molecules and clusters. The B_3^+ cluster ion which is aromatic in nature can form strong covalent bonds with inert noble gas (Ng) atoms in the $B_3Ng_3^+$ clusters. The major contributing factor in stabilizing the B-Ng bonds is the Ng \rightarrow B σ -donation. The Be-C/O bond strength and carbonyl stretching frequencies (ν_{CO}) in XBeY complexes (X = OC, CO; Y = SO₄, CO₃, O, NH, NBO, NCN) are thoroughly analyzed. The OCB₃SO₄ shows the maximum blue shift in ν_{CO} due to the strong σ -donation and weak π -back donation. The extents of the blue and red shifts have been shown to respectively depend on the strength of the σ -donation and π -back donation ability of the ligands under the study. Lewis bases including normal carbenes, mesoionic carbenes, phosphorus and nitrogen based ligands (L) can form thermochemically stable E_3L_3 complexes where the E_3 (E = Si, Ge, Sn) clusters get stabilized. The bonding interactions showed that the E-L bond is stabilized due to the L \rightarrow E σ -donation and L \leftarrow E π -back donation. The lone pair on the ligand is responsible for the L \rightarrow E σ -donation whereas the lone pair on the E atom accounts for the L \leftarrow E π -back donation. The DFT calculations show that the mesoionic carbenes (MIC) can potentially stabilize the B_2 species in $B_2(MIC)_2$ complexes. The complete electronic and thermodynamic analyses have been carried out and the results show that these MIC stabilized diborynes are comparable to the experimentally known $B_2(NHC)_2$ (NHC = N-heterocyclic carbenes). A porphyrinoid-based ligand (EP), forms stable dimagnesium(I) complex, Mg_2EP , where an Mg-Mg single bond is present. The complex show high non-linear optical (NLO) property and can behave like an electride. Furthermore, five small molecules, *viz.*, H₂, CO₂, N₂O, CH₄, and C₆H₆ are found to get activated using Mg_2EP and the associated complete reaction energy paths are explored. A metal-metal single bond at zero oxidation state of the metal atoms can be stabilized in $E_2(NHB^{Me})_2$ (E = Be, Mg; $NHB^{Me} = (HCN^{Me})_2B$) complexes. The stability of these complexes has been explored *via* the thermochemical results. The covalent nature of both metal-metal and metal-ligand bonds is explored. On a similar way, the NHB^{Me} ligand is found to form $M_2(NHB^{Me})_2$ (M = Zn, Cd, and Hg) complexes where an M-M single bond exists at the zero oxidation state of the M atoms. These complexes are mainly stabilized due to the high activation free energy barriers for the one-metal and two-metal extrusion processes.

Keywords: Donor-Acceptor Bond; Electron-Shared Bond; *Ab-Initio* Methods; Density Functional Theory; Metal-Metal Bond; Metal-Ligand Bond; Electride.