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A theoretical study on the anionic metal bis(ditholate) complexes $[M(S_2C_2R_2)_2]^{2-}$ (M=Zn(II), Cd(II), Hg(II); R=H, CH_3, CN)

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Metal bis-dithiolene complexes have indeed been the subject of extensive study by chemists in both the inorganic and organic fields in recent decades. This is due to their wide range of applications in various areas, including conducting and magnetic molecular materials, as well as their relevant optical properties [1]. Dithiolenes exist in three different forms with varying charges, which contribute to their redox activity and ability to form highly electron-delocalized complexes. However, the term dithiolene is used without taking into account the formal oxidation state of ligands to describe their noninnocent character in several metal complexes [2]. In this work, the interactions between the fragments in metal bis(1,2-dithiolate) complexes complexes $[ML_2]^{2-}$ (M=Zn(II), Cd(II), Hg(II); L= $S_2C_2H_2^{2-}$ (edt^{2-}), $S_2C_2Me_2^{2-}$ ($dmedt^{2-}$), $S_2C_2(CN)_2^{2-}$ (mnt^{2-})) have been investigated, at BP86/def2-TZVP and M06/def2-TZVP levels of theory. Four types of interaction energies between the fragments as well as the total interaction energies of the complexes [3–5] were calculated and compared. An Energy Decomposition Analysis-Natural Orbital for Chemical Valence (EDA-NOCV) was also performed to study the nature of metal−bis(dithiolate) interactions in these complexes. The results showed that among the metal complexes studied here, the Zn(II) complexes have the largest values of interaction energies. On the other hand, the values of total interaction energies of $[M(edt)_2]^{2-}$ and $[M(dmedt)_2]^{2-}$ complexes are similar or close together and both are larger than those for $[M(mnt)_2]^{2-}$ complexes. The EDA-NOCV results showed that the electrostatic interactions have considerably more contribution to the total attractive interactions compared to orbital interactions and, as expected, the contribution of dispersion forces in all complexes is inconsiderable.

Keywords: Interaction Energy, Nature of Bond, 1,2-Dithiolate Ligands, Metal Complexes.

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