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DFT study of the interaction between neutral ligands and metal cations (M = Ca^{2+}, Mg^{2+}, Li$^+$, Ni^{2+}, Pb^{2+}): Taking an insight into the interaction strength

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The interaction between organic functional groups and metal cations is largely present in proteins and play an essential role in several biological activities [1]. Alkaline and alkaline earth metal cations have fundamental role in the human body. Some metals when ingested have high toxicity and can cause several diseases. For example, nickel and lead divalent cations are present in wastewater and are toxic species to human body. Therefore, the comprehension of the qualitative and quantitative interactions between the several functional groups and the cations is of fundamental relevance. Our group has been studying a set of systems dealing with the interactions between alkaline, alkaline earth and transition metal cations with a set of functional groups, with the goal to rationalize the intensity and type of forces that control the interactions [2-8].

The B3LYP functional with a variety of basis set has been employed to quantify the interaction energy of several neutral ligands with aquacomplexes [M(H$_2$O)n]. The several terms that contribute to the stability of the complexes have been evaluated with the energy decomposition analysis (EDA) method. Correlation with empirical parameters for the functional groups has helped rationalize the main electronic features of the functional groups that modulate the interaction. The following metal cations have been studied: Li$^+$, Mg^{2+}, Ca^{2+}, Ni^{2+}, Pb^{2+}. The following functional groups were tested: phosphoryl, amide, carboxylic acid, ammonia, imine, thiocyanic acid, nitrile, amine, ammonia, thiocarbonyl, thioether, thioalcohol and phosphine. The interaction energy was quantified in terms of substitution of one water molecule in a water complex for a ligand.

Our results indicate that ligands that bind by oxygen atom have interaction energies more negative than other compounds. The interaction with alkaline and alkaline earth cations has a major electrostatic character and are favored by higher charge on the ligand atom and short distances between the metal and the ligand, typical of ionic bond. Electronic and steric effects were quantified and the most relevant contributions to the interaction energy were identified. Additionally, the influence of substituent groups on the intensity of the metal-ligand binding was also analysed. In general, electron donor groups stabilize the complexes.

This same methodology was applied for Ca^{2+} cation with dicarbonyl ligands, with each ligand substituting two water molecules. In addition to the electronic and geometric parameters previously used to rationalize the metal-ligand interaction, a new parameter called the chelating angle (the angle between the ligand atoms and the metal center) was

used, in which high values represent a gain for the stability of the formed complex. In this case the number of molecules in the product is greater than the number of molecules in the reagent so the entropic term (-TΔS) becomes relevant and contributes to the spontaneity of the reaction. The methodology was also employed for other metal cations like Pb^{2+} and Ni^{2+}. In these cases both electrostatic and covalent components are important to the metal-ligand interaction. The absolute softness of the free ligands was correlated with the covalent contribution.

Key-words: Metal-ligand interaction, DFT, Energy Decomposition Analysis

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