

UNIVERSITI TEKNOLOGI MARA

**DENSITY FUNCTIONAL THEORY
CALCULATIONS ON THE METAL-LIGAND
COMPLEXES OF Ba^{2+} , Y^{3+} AND Zr^{4+} WITH
CITRIC ACID,
ETHYLENEDIAMINETETRAACETIC ACID
AND TRIETHYLENETETRAAMINE**

NOR AIN FATHIHAH BINTI ABDULLAH

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ABSTRACT

Perovskite has been studied intensively due to its potentials in many technology-related applications such as in electrochemical devices. The effect of chelating agents was previously studied in one pot synthesis of yttrium doped barium zirconate (BZY). In this theoretical study, quantum mechanical calculations were performed to determine the relative stability of the possible structure of metal-complexation and their electronic properties. The structures were optimized using B3LYP functional with 6-31G* and Universal Gaussian Basis Set (UGBS). Three chelating agents of citric acid (CA), ethylenediaminetetraacetic acid (EDTA), and triethylenetetramine (TETA) were selected to interact with metal cations of barium (Ba^{2+}), yttrium (Y^{3+}), and zirconium (Zr^{4+}) at various strategic positions. From the calculations and considering different effects on deprotonated states, the electronic properties such as binding energies, structures, charges and molecular orbitals were recorded. The results show that the chelating agents with deprotonated 1H can bind the cations, though it interacts best with metal cations in the deprotonated 4H state. Of the three chelating agents, the highest of binding energy (E_b) was obtained in Zr^{4+} -complex (-24 eV to -45 eV) in the sequence of $\text{Zr}^{4+} > \text{Y}^{3+} > \text{Ba}^{2+}$, while Ba^{2+} rendered the least stable complex with E_b range of -18 eV to -33 eV. Atom-In-Molecules (AIM) and electron localization function (ELF) analysis show that the interaction between metal and lone pair atoms involved ionic character with values of electron density, $\rho(r)$ and Laplacian electron density, $\nabla^2\rho(r)$ ranging from 0.01 a.u to 0.2 a.u and 0.06 a.u to 0.4 a.u respectively. It was found the charge transfer occur from ligand to metal are also related to the involvement of ionic interaction between cation and lone pair atoms (oxygen/nitrogen). From molecular orbital analysis, the dominant contribution at highest occupied molecular orbital (HOMO) is from the chelating agents which composed of p orbital while at lowest unoccupied molecular orbital (LUMO) is from metals composed of s and d orbitals. In conclusion, all the chelating agents can bind the metal cations considered while they interact best in the second deprotonated states. Metal cations are favoured to attach at electron-rich sites of the chelating agents. As the size of cation affect the stability of the complexes, the larger cations of Ba^{2+} complexes preferably with TETA, while cations of Y^{3+} and Zr^{4+} with CA, EDTA and TETA. The charge transfer occurs between metal and donor atoms of chelating agents clearly shows involvement of ionic interactions in the complexes.

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