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Structural, spectral, NLO and MEP analysis of the $[MgO_2Ti_2(OPr^i)_6]$, $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$ by DFT method

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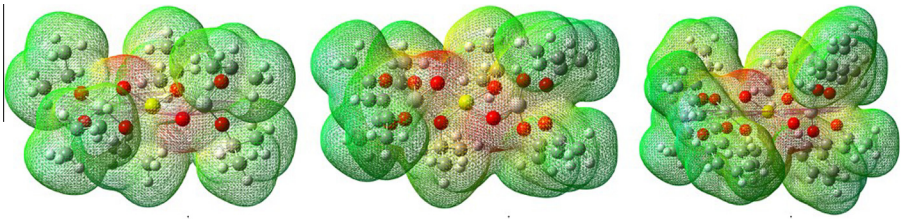
HIGHLIGHTS

- The geometrical parameters are calculated for heterobimetallic complexes.
- The complex geometry is obtained for the mentioned complexes.
- Theoretical spectroscopic studies are performed on mentioned complexes.
- The active sites and NLO properties of mentioned complexes are investigated.
- B3LYP/LANL2DZ basis set is used for all calculations.

GRAPHICAL ABSTRACT



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ABSTRACT

Quantum chemical calculations are performed on $[MgO_2Ti_2(OPr^i)_6]$ and $[MgO_2Ti_2(OPr^i)_2(L)_4]$ complexes. L is acetylacetonate (acac) and benzoylacetonate (bzac) anion. The crystal structures of these complexes have not been obtained as experimentally but optimized structures of these complexes are obtained as theoretically in this study. Universal force field (UFF) and DFT/B3LYP method are used to obtain optimized structures. Theoretical spectral analysis (IR, ^1H and ^{13}C NMR) is compared with their experimental values. A good agreement is found between experimental and theoretical spectral analysis. These results mean that the optimized structures of mentioned complexes are appropriate. Additionally, the active sites of mentioned complexes are determined by molecular electrostatic potential (MEP) diagrams and non-linear optical (NLO) properties are investigated.

Introduction

Heterometallic complexes contain two or more metal atoms in the complex structures and play an important role in biological systems, molecular magnetism and some active fields of research in chemistry [1–8]. Experimental studies in this field have been increased recently [9–18]. Magnesium titanate ($MgTiO_3$) ceramic has low dielectric loss and suitable dielectric constant. Therefore, it has been proved to be a good dielectric material [19,20]. Additionally, this ceramic has been widely applied in capacitors, resonators, filters, antennas and radars [21,22]. Magnesium titanates, magnesium silicates and magnesium aluminate are commercially produced as low dielectric components. The bimetallic μ-oxoalkoxides of transition metals have been proved to be remarkable catalyst for the polymerization of heterocyclic monomers [23]. Heterobimetallic [Mg(II)-Ti(IV)]-μ-oxoisopropoxide and its β-diketonates have been synthesized by Rajesh Kumar in 2014 [20]. Spectral and thermal analyses of these complexes have been reported as experimentally [20]. IR, ^1H- and ^{13}C-NMR spectrum of $[MgO_2Ti_2(OPr^i)_6]$ have been reported. For $[MgO_2Ti_2(OPr^i)_2(L)_4]$ type complexes, spectral analysis have not been examined in detail and crystal structures and structural

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parameters of $[MgO_2Ti_2(OPr^i)_6]$ and $[MgO_2Ti_2(OPr^i)_2(L)_4]$ complexes have not been reported.

Structural parameters and IR, UV, NMR spectrum and molecular properties can be calculated by using quantum chemical calculations. In this study, structural parameters of mentioned complexes are obtained from optimized structures. Scatter graphs are plotted by using experimental bond lengths and angles. The agreement between calculated and experimental results is explained by using correlation constant (R^2). IR, UV and NMR spectrum for mentioned complexes are calculated and compared with their experimental results. The active sites of mentioned complexes and nucleophilic activity ranking are determined by using molecular electrostatic potential (MEP) diagrams. Finally, the NLO properties of mentioned complexes are compared with each other.

Method

All computational processes of relevant complexes were made by using GaussView 5.0.8 [24], Gaussian 09 AML64-G09 Revision-C.01 programs [25]. Firstly, geometries of mentioned heterobimetallic complexes were fully optimized by using mechanics methods (UFF). After that, the geometries of mentioned complexes re-optimized at density functional theory (DFT) method which is restricted with Becke 3-parameter (exchange) Lee–Yang–Parr (B3LYP) [26,27] method with LANL2DZ [28–31] basis set. The vibration frequency analyses indicate that optimized structures of relevant complexes are at stationary points corresponding to local minima without imaginary frequencies. Time dependent-density functional theory (TD-DFT) method was used to calculate to UV–VIS spectra of mentioned complexes. The giao method was used for ^{1}H- and ^{13}C-NMR spectra. Tetramethylsilane (TMS) was selected as reference for NMR spectra.

Results and discussion

Fully optimization

The fully optimizations are performed on $[MgO_2Ti_2(OPr^i)_6]$ (**1**), $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ (**2**) and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$ (**3**) at UFF method and B3LYP/LANL2DZ level in vacuum. UFF calculations are performed to gaining job time and prevent convergence problems at B3LYP/LANL2DZ level. There are not any experimental structural parameters for complex (**1**), (**2**) and (**3**). The optimized structures and some calculated structural parameters of mentioned complexes are given in Fig. 1 and Table 1, respectively. Hydrogen atoms are omitted at Fig. 1 for clarity.

According to the Table 1, there are four coordinate-covalent bonds around the magnesium (II) ion. The bonds which are Mg–O_2 and Mg–O_3 are stronger than Mg–O_1 and Mg–O_4 in $[MgO_2Ti_2(OPr^i)_6]$ complex. As for the $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$ complexes, the Mg–O bond strengths are close to each other. There are four metal – oxygen (M–O) bonds around each Ti(IV) metal. As seen from Fig. 1, the complex geometry of Mg(II), Ti(IV) metals is distorted tetrahedral for complex (**1**). In complex (**2**) and (**3**), there are four M–O bond around magnesium(II) metal. The bond lengths are close to each other. Therefore, bond strengths of these M–O bonds is close to each other. As for the titanium(IV) metals, there are six bonds around metal ions. This result means that the complex geometries around the Ti(IV) metals is distorted octahedral while the complex geometry around the Mg(II) metal ion is distorted tetrahedral. Input file of $[MgO_2Ti_2(OPr^i)_6]$, $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$ complexes are given as Supplemental material.

The harmonic vibration frequencies are calculated at same level of theory in vacuum. The harmonic frequencies are scaled by 0.96 [32,33] to obtaining anharmonic frequencies. The calculated anharmonic frequencies and theirs experimental values are subjected to correlation analysis and correlation constant (R^2) values are calculated for each correlation analysis. The anharmonic vibration frequencies are given in Table 2.

According to the Table 2, there is a good agreement between experimental and calculated vibration frequencies. The metal–oxygen frequencies have been given as 700–400 cm^{-1} [20]. Ti–O frequencies are calculated as 848, 860 and 858 cm^{-1} while Mg–O frequencies are obtained as 536, 579 and 582 cm^{-1} for $[MgO_2Ti_2(OPr^i)_6]$, $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$, respectively. As experimentally, the vibration frequencies of $[MgO_2Ti_2(OPr^i)_2(L)_4]$ have been obtained by Rajesh Kumar in 2014 [20]. Common frequencies have been given in Ref. [20] for $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$ complexes. In this study, the vibration frequencies are calculated for each

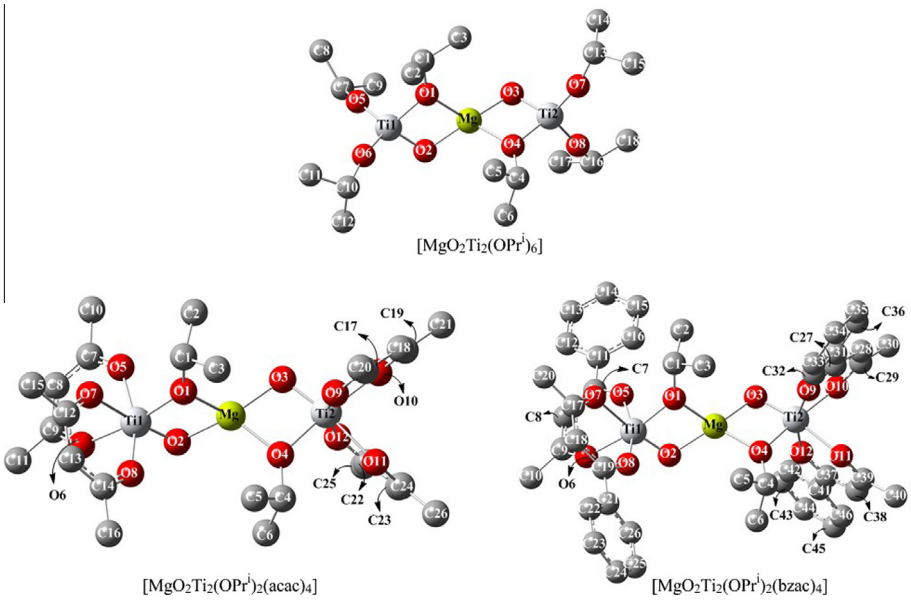

Fig. 1. Optimized structures of $[MgO_2Ti_2(OPr^i)_6]$, $[MgO_2Ti_2(OPr^i)_2(acac)_4]$ and $[MgO_2Ti_2(OPr^i)_2(bzac)_4]$ at B3LYP/LANL2DZ level in vacuum with atomic labelling.