

Poster Presentations

[MS24-P02] Structural and Theoretical Studies of Two Novel Sandwich Type 2D Silver(I) Coordination Polymers Built up by Aromatic and Aliphatic Di-carboxylic acid
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The rational design and synthesis of metal-organic coordination polymers (MOCPs) have been attracted great interest not only due to their intriguing variety of structures but also to their potential applications in materials science such as gas storage, luminescent materials, magnetic materials, catalysis, non-linear optics (NLO) [1-5]. Especially, among MOCPs, the d^{10} silver(I) coordination polymers have received great attention in the last two decades as being one of the most interesting research fields in supramolecular coordination chemistry due to the flexible coordination geometries varying from linear to trigonal, tetragonal, square pyramidal, and octahedral, corresponding to coordination numbers ranging from 2 to 6 [6]. As we know that multifunctional carboxylate ligands have gained a great attention in coordination chemistry owing to their diversity bridging capacity. Among of them, aromatic and aliphatic dicarboxylate ligands have been widely used as building blocks in the fabrication of organic-inorganic hybrid materials with desired topologies [7-9]. In this study, two 2D silver(I) coordination polymers constructed from aromatic and aliphatic dicarboxylic acid have been synthesized under classical conditions and structurally characterized by elemental analysis, infrared spectroscopy (IR) and single crystal X-ray diffraction techniques. X-ray crystallographic study reveals that complexes 1 and 2 represent two-dimensional (2D) coordination polymer with metal-organic sandwich type and two independent Ag(I) ions are linked to constructed 2D layer by $\mu^8-\eta^3:\eta^2:\eta^2:\eta^1$ (for complex 1) and $\mu^7-\eta^3:\eta^2:\eta^2:\eta^2$ (for

complex 2) coordination modes (Fig. 1).

The 2D layers of 1 are further extended into a three-dimensional (3D) supramolecular network by short Cl \cdots Cl interactions while 2D layers of 2 are linked by CH \cdots O interactions into a 3D supramolecular framework. Moreover, two complexes exhibit considerable short Ag-Ag argentophilic interactions.

Natural bond orbital (NBO) and frontier molecular orbital (FMO) analyses were carried out by using the density functional theory (DFT) method in order to elucidate the information regarding intra-molecular charge transfer within the complexes. The X-ray crystal structures of complex 1 and complex 2 were used as starting structures for NBO and FMO analyses due to difficulty of carrying out geometry optimization with quantum chemical methods for such large systems. The NBO analysis reveals appreciable donor-acceptor type delocalization from lone-pair (n) of oxygen orbitals with anti-lone-pair (n^*) of metal orbitals. The delocalization effects due to nn^* interactions in the complex 1 and complex 2 play a highly important role on the coordination environments of the silver atom. The 3D plots of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for complex 1 and complex 2 were shown in Fig. 2. According to the calculated HOMO-LUMO energies with different DFT functional and basis set, gap energy of complex 1 was bigger than that of complex 2 for both B3LYP and M06 functional.

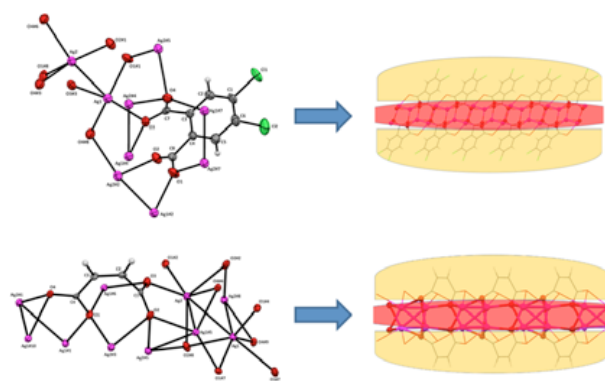


Fig. 1. The crystal structures and metal-organic sandwich models of complexes 1 and 2.

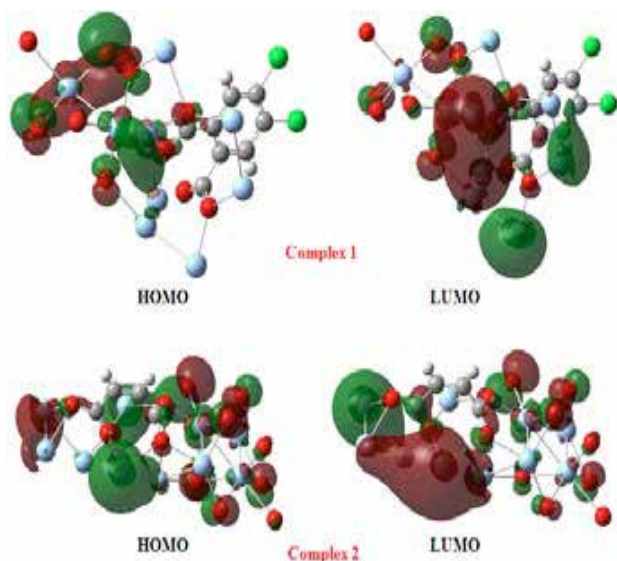


Fig. 2. The frontier molecular orbitals of 1 and 2 obtained with M06 functional and GenECP (6-31g(d,p) and SDD) basis set (positive and negative lobes of orbitals are shown with red and green, respectively).

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