

MS29-1-1 Structure-directing Ag $\cdots\pi$ interactions in coordination complexes

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T. Theunissen¹, S.A. Bourne¹, C. Esterhuysen²¹University of Cape Town - Cape Town (South Africa), ²University of Stellenbosch - Stellenbosch (South Africa)**Abstract**

The Ag- π interaction can be considered as one of the most widely used metal- π interactions [1]. The interactions have been applied to a number of fields, including catalysis [2], molecular recognition [3], and polymer/material design [4]. In spite of the usefulness of Ag- π interactions, a better understanding of the orbital interactions that govern the stability trends is still required. This information could assist in guiding design of new materials and applications that exploit this interaction.

The reaction of silver(I) nitrate with sodium benzoate (NaBn) and a pyridyl yielded three binuclear complexes: [Ag₂(Bn)₂] (I) and [Ag₂(Bn)₂(2-Pic)₂] (II) and [Ag₂(Bn)₂(3-ClPic)₂] (III) where 2-Pic is 2-picoline and 3-ClPic is 3-chloropyridine. All three of these complexes have been characterized by IR, thermal analysis, and X-ray single crystal and powder diffraction. Complexes (I), (II), and (III) are all linked into Ag-Ag (<2.885 Å) dimers with the silver(I) ions being bridged by the benzoate ligands. Additionally, complexes (II) and (III) each had the silver(I) ion bound to one monodentate picoline-derived ligand. Complex (I) packs as a two-dimensional polymer structure, while complexes (II) and (III) each form one-dimensional chains connected by weak intermolecular interactions. These weak intermolecular Ag $\cdots\pi$, $\pi\cdots\pi$, and H $\cdots\pi$ interaction systems are expected to lead to the assembly and by extension the stability of the three-dimensional crystal frameworks. The nature of these interactions, namely the Ag $\cdots\pi$, was further examined by DFT calculations. The Ag $\cdots\pi$ interactions were found to be driven by favourable molecular orbital interactions, between an aromatic π -donor orbital and the Ag LP* acceptor orbital (a π) \rightarrow LP* interaction). The Ag $\cdots\pi$ interactions displayed the classical preferential alignment of the Ag LP* toward the ring carbons and/or nitrogen and an aromatic π orbital rather than toward the aromatic centroid. These results describe a potential understanding of the weak interactions of silver(I) with π systems.

References

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Silver(I) complexes with benzoate and pyridines

