



Crystal structures and supramolecular architectures of ONO donor hydrazone and solvent exchangeable dioxidomolybdenum(VI) complexes derived from 3,5-diiodosalicylaldehyde-4-methoxybenzoylhydrazone: Hirshfeld surface analysis and interaction energy calculations

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ABSTRACT

A tridentate ONO donor aroylhydrazone, 3,5-diiodosalicylaldehyde-4-methoxybenzoylhydrazone (H₂DSMB), and two of its *cis*-MoO₂ complexes, [MoO₂(DSMB)(H₂O)](DMF)₂ (**1**) and [MoO₂(DSMB)(py)] (**2**), have been synthesized and characterized by different physico-chemical methods. The molecular structures were determined by single crystal X-ray diffraction studies. The aroylhydrazone H₂DSMB crystallizes in a monoclinic space group with two identical molecules in the asymmetric unit. The complex [MoO₂(DSMB)(H₂O)](DMF)₂ (**1**) crystallizes in a triclinic space group whereas the other complex, [MoO₂(DSMB)(py)] (**2**), crystallizes in an orthorhombic crystal system. The distorted octahedral geometry around the Mo(VI) central atom is satisfied by the di-deprotonated dianionic hydrazone moiety and two oxido oxygen atoms, the sixth labile coordination site being occupied by oxygen/nitrogen atoms from solvent molecules. The importance of van der Waals interactions in the formation of the elementary structure obtained from the single crystal X-ray diffraction was authenticated by Hirshfeld surface analysis. The individual types of intermolecular contacts and their impact on the crystal packing was investigated by the analysis of the Hirshfeld surfaces and the signatures on the two-dimensional fingerprint plots. Interaction energy calculations reveal that the dispersion energy framework is dominant over other energy frameworks. The thermal behavior and the nature of the water molecule in the complex [MoO₂(DSMB)(H₂O)](DMF)₂ (**1**) is discussed. Furthermore, *in vitro* cytotoxicity studies of the synthesized aroylhydrazone and its Mo(VI) complexes against the lymphoma ascites cell line are also included.

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1. Introduction

The inherent ability of hydrazones to act as building blocks together with various metals makes them potential candidates for producing metal complexes with diverse topologies [1]. The well-known chelating ability and structural flexibility allows hydrazone ligands to occupy a special position among such ligand systems. Aroylhydrazones and their transition metal complexes have also experienced explosive growth owing to their pioneering applications in multifarious fields [2–7].

Depending on reaction parameters, such as pH of the medium, the metal ion and its concentration, the nature, denticity and

ability of the hydrazone ligands to exhibit keto-enol tautomerism, the resulting complexes display versatile coordination modes with unusual coordination numbers [8]. Moreover, the final structures of the complexes are determined by several factors, including the nature and geometrical disposition of the donor sites, the effect of counter ions and the presence of various non-covalent interactions. Metal complexes involving supramolecular interactions are an area of special interest. The bases for the design of supramolecular architecture leading to complicated crystal packing are non-covalent interactions. In addition to this, the coordination geometry of the metal and the orientation of the coordination sites also play a key role. Non-covalent interactions include weaker interactions (≤ 4 kcal/mol), such as C–H $\cdots\pi$, $\pi\cdots\pi$, metal $\cdots\pi$ etc. These interactions provide additional stability to the crystal structure.

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