



Cd(II) and Ni(II) complexes from a tridentate NNO Schiff base: Crystal structures, spectral aspects and Hirshfeld surface analysis

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ABSTRACT

A tridentate NNO donor Schiff base, 2,4-dichlorido-6-((3-(dimethylamino)propylimino)methyl)phenol (HL) and its three complexes [CdL₂·H₂O] (1), [NiL₂] (2) and [NiLL'(DMF)] (3) (HL' = 3,5-dichlorosalicylaldehyde) were synthesized and physicochemically characterized by means of elemental analysis, molar conductivity measurements, FT-IR, UV-Vis and NMR spectral studies. The molecular structures of all three complexes were confirmed by X-ray crystallography. In all three complexes, the metal ions are in distorted octahedral environments. [CdL₂·H₂O] (1) crystallized in a triclinic space group, whereas both [NiL₂] (2) and [NiLL'(DMF)] (3) crystallized in the monoclinic crystal system. The crystal structures of the complexes exhibit different types of intermolecular interactions, which have been supported by Hirshfeld surface analysis and associated fingerprint plots. The luminescent properties of the Schiff base and the three complexes were studied, and the nature of the emission was found to be quenching.

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1. Introduction

The role of Schiff bases in the advancement of coordination chemistry is invaluable. The potential applications of metal complexes of Schiff bases in the field of bioinorganic chemistry [1–3], catalysis [4], medicinal chemistry [5] and material science [6] make them considerably relevant. The structural varieties and interesting properties have also augmented their importance. As all three donor sites can coordinate to a metal ion, NNN, NNO and ONO donor type Schiff base ligands have received tremendous attention in this field of chemistry [7,8]. The synthesis of transition metal complexes with aldehydes as a co-ligand is a topic of utility concern, since the aldehydic group can undergo different kinds of chemical reactions [9]. Such mixed ligand complexes have enormous applications in the fields of biochemistry [10] and analytical chemistry [11].

Schiff base complexes are also broadly studied for their unique self-assembling nature and their ability to form unexpected supramolecular architectures [12]. The interplay of weak non-covalent interactions, namely π - π , C-H \cdots π , lone pair \cdots π , halogen interactions, unconventional hydrogen bonds etc., in addition to hydrogen bonding interactions, in the formation of supramolecules

needs to be specified [13]. The quantification of intermolecular forces, which aids in acquiring more information regarding the crystal structure and stability, is of great importance and the increase in the number of publications which include this concept validates this. A powerful tool in this regard is the calculation of a molecular Hirshfeld surface [14]. A Hirshfeld surface is a 3D surface which is unique for each crystal and provides an insight into structural aspects of crystal systems. A 2D fingerprint plot generated from this can deconstruct the atom pair contacts and quantitatively summarize the intermolecular interactions [15].

In this present endeavor, we report the synthesis and characterization of an N₂O donor tridentate Schiff base [HL], derived by refluxing N,N-dimethyl-1,3-diaminopropane and 3,5-dichlorosalicylaldehyde, and three new Cd(II) and Ni(II) complexes of the same. Of these complexes, [CdL₂·H₂O] (1) and [NiL₂] (2) are bisligated and [NiLL'(DMF)] (3) is a mixed ligand complex in which three of the coordination sites are satisfied by the reactant aldehyde (HL') itself and a solvent molecule. A bisubstituted amine is chosen for studying the role of other weak interactions in forming the supramolecular architectures by suppressing the hydrogen bonding interactions of the resulting tridentate Schiff base. Crystal structures and supramolecular aspects are discussed. The quenching nature in the emission profiles of the ligand and the metal complexes are also studied.

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