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# CRYSTAL STRUCTURE, AND HIRSHFELD SURFACE ANALYSIS OF A POLYMERIC Mn(II)COMPLEX WITH 4-AMINOBENZOIC ACID

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## Introduction

Para-aminobenzoic acid (PABA) has garnered significant interest in coordination chemistry due to its ability to form stable complexes with various metal ions. Among these, manganese (Mn) stands out as a versatile metal that can adopt multiple oxidation states and coordination geometries, making it an attractive candidate for synthesizing novel polymeric structures. The incorporation of PABA into Mn complexes not only enhances the stability of the coordination framework but also introduces potential applications in fields such as catalysis, drug delivery, and materials science [1]. Manganese complexes with PABA exhibit unique structural features that influence their properties and functionality. The presence of carboxylate and amino functional groups in PABA facilitates strong coordination interactions with Mn ions, leading to the formation of intricate polymeric networks. These networks often display interesting magnetic, electronic, and optical properties, driven by the interplay between the metal centers and the organic ligand [2]. In recent studies, the synthesis and characterization of Mn-PABA polymeric complexes have revealed promising results, showcasing their potential for various applications. Understanding the structural and electronic properties of these complexes can pave the way for the development of advanced materials with tailored functionalities. This introduction aims to provide an overview of the significance of PABA in Mn coordination chemistry and the potential implications of Mn-PABA polymeric complexes in diverse scientific domains [3].

## Single crystal X–ray structure analysis

An asymmetric portion of the triclinic unit cell comprises two complex molecules of independent Mn ions and one uncoordinated water molecule (Fig. 1a).

The $Mn1^{+2}$ and $Mn2^{+2}$ ions are positioned at inversion centers and have identical configurations of their coordination spheres. The ligand molecules are in a benzoate form, with two PABA molecules and two water molecules coordinated to the metal ions. The coordination of these ligand molecules occurs through the oxygen atoms of the carboxylate groups in a monodentate fashion. Two nitrogen atoms generated by symmetry operations occupy the remaining positions in the coordination sphere (Fig. 1a). The Mn–O bond lengths range from 2.072(3) to 2.224(3) Å and from 2.075(3) to 2.213(3) Å, while the Mn–N distances are 2.224(3) and 2.213(3) Å for the Mn1 and Mn2 ions, respectively (Table 3). Consequently, the bond angles vary from 84.89(9)° to 95.11(9)° for the Mn1 polyhedron and from 86.59(9)° to 93.41(9)° for the Mn2 polyhedron (Table 3). Thus, the coordination polyhedra are distorted octahedra. The planes of the carboxylate groups of the ligand molecules linked to the Mn1 and Mn2 ions are tilted at angles of 9.77(9)° and 9.16(9)° relative to their respective aromatic rings. Two antiparallel PABA molecules connect neighboring Mn atoms through coordination bonds involving N and O atoms, resulting in infinite polymeric columns extending along the b-axis (Fig. 1b). The structures of the columns containing the Mn1 and Mn(II) ions (Mn Co-columns) are similar, but they are twisted by 22.34(10)° with respect to one another due to packing requirements. There are no significant π-π interactions between the antiparallel aromatic rings of the columns, as the distances between the centroids of the rings are 4.132(3) Å and 3.985(3) Å for the Mn1 and Mn2 columns, respectively. The crystal structure is characterized by a complex system of intra- and intermolecular hydrogen bonds. In both columns, the coordinated water molecules O1W and O2W are hydrogen-bonded to the uncoordinated oxygen atoms O2A and O2B of the carboxylate groups, represented by the graph-set notation $S_1^1(6)$ [16]. The hydrogen bonds O3W–HO1B and O3W–N2A from the uncoordinated water molecule (Fig. 2; Table 4), along with symmetrically related ones, link the Mn2 columns into a 2-D network, forming a graph-set with $R_4^4(20)$ notation. The formation of larger cycles through hydrogen bonds O2W–HO2A and O1W–HO2B, which correspond to a graph-set of $R_4^4(24)$, integrates the columns of both metal ions into a 3-D structure. The hydrogen bond O3W–HO2A further enhances the 3-D network or contributes to the formation of larger hydrogen bond cycles. There are weak π-π interactions between the aromatic rings of the Mn2 columns aligned along the x-axis, with a centroid distance of 3.859 Å. However, such interactions do not occur in the packing of the Mn1 columns, where the corresponding distance increases to 4.580 Å.

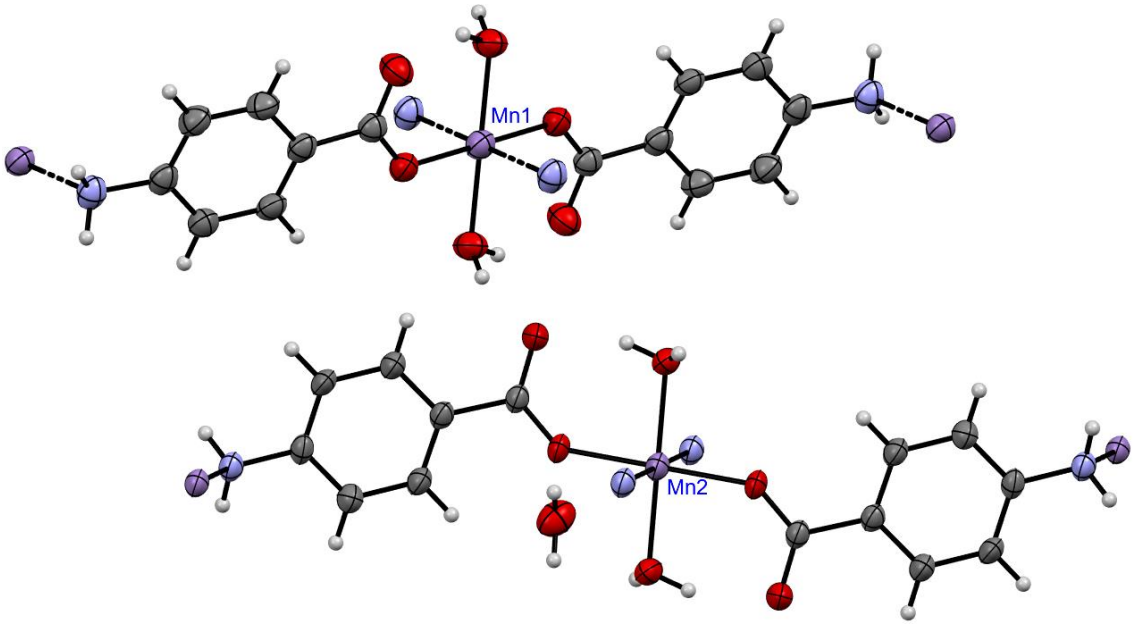


**Figure 1.** Molecular structure of Complex I.

**Analysis Hirshfeld surfaces.**

To compute the Hirshfeld surfaces and their corresponding 2D fingerprint diagrams, we utilized the Crystal Explorer 21.5 software, which requires files in CIF format [1]. The Hirshfeld surface is defined as the outer boundary of the space occupied by a molecule or atom in a crystalline medium. For each point on the iso-surface, two distances are indicated: di, the distance to the nearest nucleus within the surface, and de, the distance to the nearest atoms outside the surface. The normalized contact distance (dnorm), which is based on the atom's de and di values and their van der Waals (vdW) radii, can be calculated using a specific equation. This calculation helps identify areas important for interactions, where $r_i^{vdW}$ and $r_e^{vdW}$ represent the van der Waals radii of the inner and outer atoms relative to the surface, respectively. The dnorm value is either negative or positive, depending on whether the intermolecular bonds are shorter or longer than the van der Waals radii.

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}} \quad (1).$$

The $\boldsymbol{d_{norm}}$ parameter is visually depicted on the Hirshfeld surface through a color gradient ranging from red to white to blue. The bright red regions indicate intermolecular contacts occurring within a distance shorter than the respective van der Waals radii, while the blue regions signify intermolecular contacts at distances greater than the van der Waals radii. The white regions correspond to the cumulative van der Waals radii for the associated atoms.

Normalized contact distances of the Hirshfeld surfaces of the coordination compound were calculated using a neutral whole molecule. The Hirshfeld surfaces were observed at distances ranging from -0.4817 to 1.2479. Analysis revealed that the volume of the Hirshfeld surface cavity measures 592.66 Å³, while the surface area occupied is 501.56 Å² (Fig. 1).

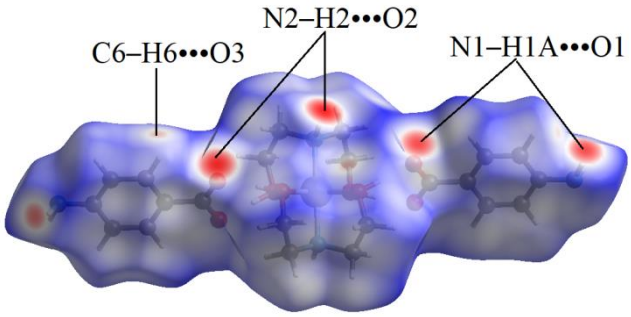


**Fig 2. Hirshfeld surface of the compound, interactions within and outside the surface ($d_{norm}$).**

The Hirshfeld surface shape index comprises curved depressions and convexities, which are observed at distances ranging from -0.9967 to 0.9932 atomic sizes. The shape index analysis indicated a partial parallel arrangement of molecular segments (aromatic rings), leading to a π-π overlap effect (Fig. 2).

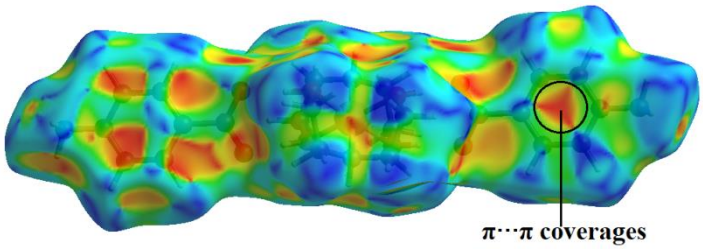


**Figure 3. Shape index curvatures and π-π coverage of the Hershfeld surface**

Analysis of 2D fingerprint patterns of the Hirshfeld surface of the complex revealed six types of homo- and heteroatomic bond interactions that contribute to the overall crystal packing within and between molecules. The most prominent intermolecular interactions in the formation of the Hirshfeld surface were H---H and H---O/O---H, which contributed 60.3% and 18% respectively to the formation of the Hirshfeld surface. Another significant contribution comes from H---C interaction, which accounts for 15.3% of the surface formation. To a lesser extent, the interaction of C---C atoms contributes to the formation of the Hirshfeld surface with 2.6%, H---N/N---H interactions with 2.3%, and N---C/C---N with 1.6% (Fig. 3).

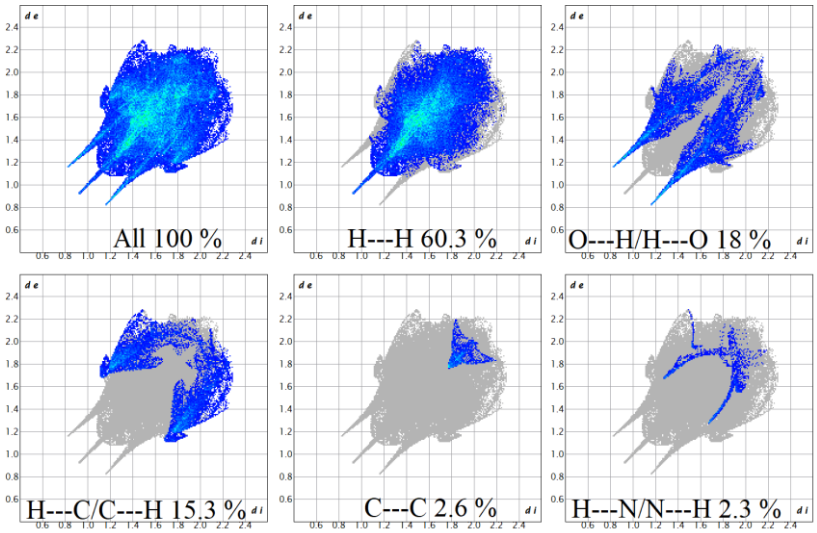


**Figure 4. Fingerprint image of the Hirshfeld surface of the compound, contributions of interatomic interactions to surface formation.**

**References**

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