

Impact Factor:	ISRA (India)	= 6.317	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
	ISI (Dubai, UAE)	= 1.582	ПИИИ (Russia)	= 0.191	PIF (India)	= 1.940
	GIF (Australia)	= 0.564	ESJI (KZ)	= 8.100	IBI (India)	= 4.260
	JIF	= 1.500	SJIF (Morocco)	= 7.184	OAJI (USA)	= 0.350

SOI: [1.1/TAS](#) DOI: [10.15863/TAS](#)

International Scientific Journal
Theoretical & Applied Science

p-ISSN: 2308-4944 (print) e-ISSN: 2409-0085 (online)

Year: 2024 Issue: 11 Volume: 139

Published: 28.11.2024 <http://T-Science.org>

Issue

Article



A.S. Normamatov

Institute of General and Inorganic Chemistry, Uzbekistan Academy of Sciences
M.Ulugbek Str., 77a, Tashkent 100170, Uzbekistan

B.T. Ibragimov

Institute of Bioorganic Chemistry, Uzbekistan Academy of Sciences
M.Ulugbek Str., 83, Tashkent, 100125, Uzbekistan

A.B. Ibragimov

Institute of General and Inorganic Chemistry, Uzbekistan Academy of Sciences
M.Ulugbek Str., 77a, Tashkent 100170, Uzbekistan
aziz_ibragimov@mail.ru

P.K. Kodamboev

Khorezm Mamun academy, Uzbekistan Academy of Sciences
Uzbekistan Khorezm 220900 Khiva, Markaz-1

A.Sh. Juraev

Institute of General and Inorganic Chemistry, Uzbekistan Academy of Sciences
M.Ulugbek Str., 77a, Tashkent 100170, Uzbekistan

COORDINATION POLYMER OF CU (II) WITH 5-SULFOSALYSLIC ACID AND MONOETHANOLAMINE: SYNTHESIS, STRUCTURE AND HIRSHFELD SURFACE ANALYSIS

Abstract: A novel coordination polymer (CP) has been synthesized and characterized through a combination of techniques including elemental analysis, Fourier Transform Infrared (FT-IR) spectroscopy, X-ray crystallography, and Hirshfeld surface analysis. The compound, formulated as $[\text{Cu}_2(\text{SSA})_4]_n(\text{MEA})_2(\text{H}_2\text{O})_4$, exhibits a distinctive "paddle-wheel" or "Chinese lantern" structural motif. In this structure, copper ions occupy the central axis, while sulphosalicylic acid (SSA) ligands bridge these metal centers, forming a polymeric chain. The SSA molecules coordinate to the copper ions in two distinct ways axial coordination: The oxygen atoms (O10) of the sulfo groups bind to the metal centers. Equatorial coordination: The carboxylate ends of the SSA molecules link neighboring paddle-wheel units, resulting in the formation of polymeric chains extending along the [100] direction. Intramolecular hydrogen bonding (O1-H...O5) is observed within the SSA molecules. A Hirshfeld surface analysis was conducted to gain insights into the intermolecular interactions within the crystal structure. The analysis reveals significant variations in the contributions of different elements to both the internal and external surfaces of the molecule: Hydrogen: Makes substantial contributions to both the internal (31%) and external (59.7%) surfaces. Oxygen: Plays a significant role in the internal surface (49%) but a lesser role in the external surface (29.5%). Carbon: Contributes moderately to the internal surface (15.9%) and minimally to the external surface (6.1%). Copper: Has a minor impact on both internal (4.1%) and external (4%) surfaces. These findings provide valuable information about the packing arrangement and intermolecular interactions within the crystal lattice of the coordination polymer.

Key words: coordination polymer, Hirshfeld surface, oxygen.

Language: English

Impact Factor:

ISRA (India)	= 6.317	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
ISI (Dubai, UAE)	= 1.582	PIIHQ (Russia)	= 0.191	PIF (India)	= 1.940
GIF (Australia)	= 0.564	ESJI (KZ)	= 8.100	IBI (India)	= 4.260
JIF	= 1.500	SJIF (Morocco)	= 7.184	OAJI (USA)	= 0.350

Citation: Normamatov, A.S., Ibragimov, B.T., Ibragimov, A.B., Kodamboev, P.K., & Juraev, A.Sh. (2024). Coordination polymer of CU (II) with 5-sulfosalicylic acid and monoethanolamine: synthesis, structure and hirshfeld surface analysis. *ISJ Theoretical & Applied Science*, 11 (139), 377-383.

Soi: <http://s-o-i.org/1.1/TAS-11-139-41>

Doi:  <https://dx.doi.org/10.15863/TAS.2024.11.139.41>

Scopus ASCC: 1604.

Introduction

Sulfosalicylic acid (SSA) forms stable complexes with a variety of metal ions, finding applications in analytical chemistry, medicine, and materials science [1]. These complexes exhibit diverse properties and functionalities, including colorimetric detection of metal ions, chelation therapy, drug delivery, and catalysis [2]. The stability, sensitivity, and selectivity of SSA complexes make them valuable tools in various fields. However, further research is needed to address potential toxicity concerns and enhance their stability in biological environments [3, 4].

One of the most prominent applications of SSA complexes is in analytical chemistry. The formation of colored complexes with several metal ions, such as iron(III), titanium(IV), and vanadium(V), allows for their spectrophotometric determination [5]. This property is exploited in various analytical techniques, including colorimetric titrations and spectrophotometric assays. Additionally, SSA can serve as a primary standard in acid-base titrations due to its high purity and stability [6].

Materials science is another area where SSA complexes have found utility. The ability of SSA to form stable complexes with metal ions has been exploited in the development of metal ion sensors [7]. By incorporating SSA into sensor materials, it is possible to detect and quantify metal ions in various samples, including water and environmental samples. Additionally, SSA complexes have been used as catalysts and catalyst supports in various chemical reactions [8]. The unique properties of SSA complexes, such as their ability to stabilize metal ions and promote electron transfer, make them attractive candidates for catalytic applications [9]. Despite these challenges, the versatility and potential of SSA complexes make them a promising area of research. Ongoing research efforts are focused on developing new and improved SSA complexes with enhanced properties and applications [10]. By addressing the limitations and exploring new opportunities, researchers aim to unlock the full potential of SSA complexes in various fields, from analytical chemistry to medicine and materials science [11].

Synthesis of the complex

0.508 g (2 mmol) of 5-sulfosalicylic acid dihydrate was dissolved in 40 mL of ethanol, and then 61 μ L (1 mmol) of monoethanolamine was added, mixing thoroughly (solution I). Next, 0.207 g (1

mmol) of $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 30 mL of water (solution II). Solution II was then slowly added to solution I while stirring, resulting in a clear, transparent green solution (pH = 4). The container was placed in a thermostat at a constant temperature of 22 °C to allow for solvent evaporation. After 10 days, light green crystals appeared. Yield: 75%. Elemental analysis: calculated 32.43% (C), 3.04% (H), 2.36% (N), 10.81% (S), 40.54% (O); experimental 32.11% (C), 2.97% (H), 2.16% (N), 10.34% (S), 39.84% (O).

Crystal structure

A polymeric paddle-wheel copper complex forms upon crystallization from a media containing 5-sulfosalicylic acid (SSA), monoethanolamine (MEA), and the salt $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Paddle-wheel metal complexes are a class of coordination compounds characterized by a unique binuclear core structure. This core consists of two metal ions (often transition metals) held in close proximity by four bridging ligands. The general formula for these complexes is $[\text{M}_2(\text{L}1)_4(\text{L}2)_2]$, where M - metal ion, L1 - chelating equatorial ligand (typically carboxylate) and L2 - axial ligand. The L1 ligands coordinate to both metal ions in a bidentate mode, forming a planar, rectangular arrangement. Typically, these complexes exhibit inversion symmetry, with the inversion center located midway between the two metal ions. Each metal ion adopts a square pyramidal coordination geometry.

The name "paddle-wheel" is derived from the visual resemblance of this core structure to an old-fashioned paddle wheel, with the metal ions representing the axle and the bridging ligands forming the paddles. Alternatively, it is sometimes referred to as a "Chinese lantern" structure [12].

Paddle-wheel complexes exhibit a wide range of properties and applications. A significant number of these complexes (1571), particularly those involving copper, manganese, zinc, cobalt, chromium, nickel, rhodium, and other metals with carboxylic acids, are documented in the Cambridge Structural Database (CSD) [13]. Approximately half of these complexes are copper-based, and a substantial portion involves benzoic acid derivatives. Among the copper-benzoic acid derivative complexes (280), nearly a quarter (78) feature water molecules as axial ligand. This prevalence suggests that copper-based paddle-wheel complexes with axial water molecules are particularly common. However, no paddle-wheel metal complexes of SSA are found in the CSD, despite the registration of its some coordination polymers. [14].

Impact Factor:	ISRA (India)	= 6.317	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
	ISI (Dubai, UAE)	= 1.582	ПИИИ (Russia)	= 0.191	PIF (India)	= 1.940
	GIF (Australia)	= 0.564	ESJI (KZ)	= 8.100	IBI (India)	= 4.260
	JIF	= 1.500	SJIF (Morocco)	= 7.184	OAJI (USA)	= 0.350

Table 1. Crystal data and structure refinement

Empirical formula	C ₁₆ H ₁₈ CuNO ₁₅ S ₂
Formula weight	591.97
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4173(2)
b/Å	10.3633(2)
c/Å	14.1364(2)
α/°	95.029(2)
β/°	90.4340(10)
γ/°	109.150(2)
Volume/Å ³	1297.30(4)
Z	2
ρ _{calc} /cm ³	1.515
μ/mm ⁻¹	3.329
F(000)	604.0
Crystal size/mm ³	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.282 to 142.916
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 12, -17 ≤ l ≤ 17
Reflections collected	12534
Independent reflections	4983 [R _{int} = 0.0242, R _{sigma} = 0.0271]
Data/restraints/parameters	4983/0/327
Goodness-of-fit on F ²	1.083
Final R indexes [I > 2σ (I)]	R ₁ = 0.0604, wR ₂ = 0.1882
Final R indexes [all data]	R ₁ = 0.0638, wR ₂ = 0.1930
Largest diff. peak/hole / e Å ⁻³	2.65/-0.80

In our case, SSA molecules coordinate to the axial positions (L1=L2), forming a polymeric paddle-wheel complex. The formula of the compound is [Cu₂(SSA)₄]_n(MEA)₂(H₂O)₄ (Fig.1).

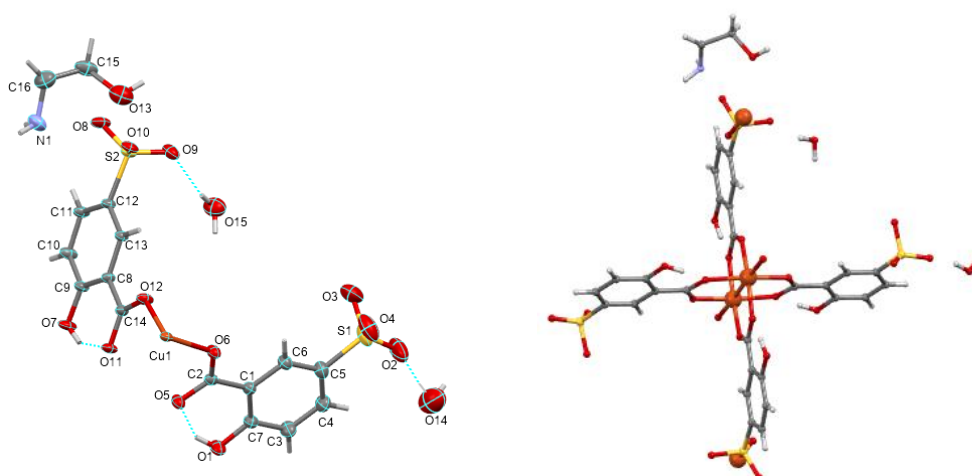


Figure 1. Asymmetric part of the crystal structure (left) and formation of the paddle-wheel complex (right) (ligands in axial positions are not shown).

Impact Factor:

ISRA (India) = 6.317
ISI (Dubai, UAE) = 1.582
GIF (Australia) = 0.564
JIF = 1.500

SIS (USA) = 0.912
ПИИИ (Russia) = 0.191
ESJI (KZ) = 8.100
SJIF (Morocco) = 7.184

ICV (Poland) = 6.630
PIF (India) = 1.940
IBI (India) = 4.260
OAJI (USA) = 0.350

In axial positions, also SSA molecules are coordinated through the O10 oxygen atom of the sulfo-group. The carboxylate end of this molecule coordinates with a neighboring paddle-wheel molecule, resulting in the formation of polymeric

columns extending along the [100] direction. There is intramolecular H-bonds O1-H...O5 in the SSA molecules. This hydroxy group O1-H is also H-bonded to O9 atom of the SSA molecule coordinated in axial position (Fig. 2).

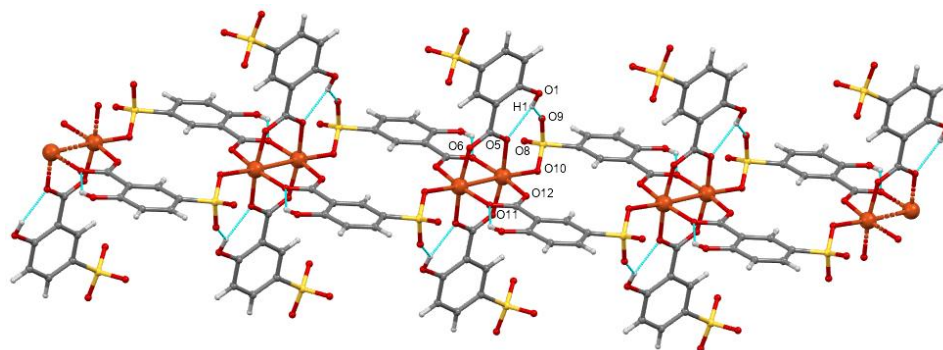


Figure 2. Polymeric column of the compound parallel to the [100] direction.

There are complicated intermolecular H-bonds between complex molecules, MEA and 2 water molecules (Table 2). These H-bonds incorporate these

fragments into 2-D network parallel (101) plane (Fig. 3).

Table 2. Hydrogen bonds in the crystal structure.

D-H...A	D-H, Å	H...A, Å	D...A, Å	< D-H...A, °	Symmetry
O1-H1...O5	0.8200	1.9300	2.601(4)	138.00	
O1-H1...O9	0.8200	2.2400	2.847(4)	131.00	1+x,y,z
N1-H1A...O10	0.8700	2.1800	3.029(5)	167.00	-x,2-y,-z
O7-H7...O8	0.8200	2.4800	2.954(4)	118.00	1+x,y,z
O7-H7...O11	0.8200	1.9400	2.628(4)	141.00	
O14-H14A...O2	0.8500	2.0200	2.840(8)	161.00	
O14-H14B...O9	0.8500	2.2700	3.005(9)	146.00	x,1-y,1-z
O15-H15D...9	0.8500	2.0500	2.873(5)	164.00	
C6-H6...N1	0.9300	2.5500	3.420(6)	156.00	x,-1+y,z

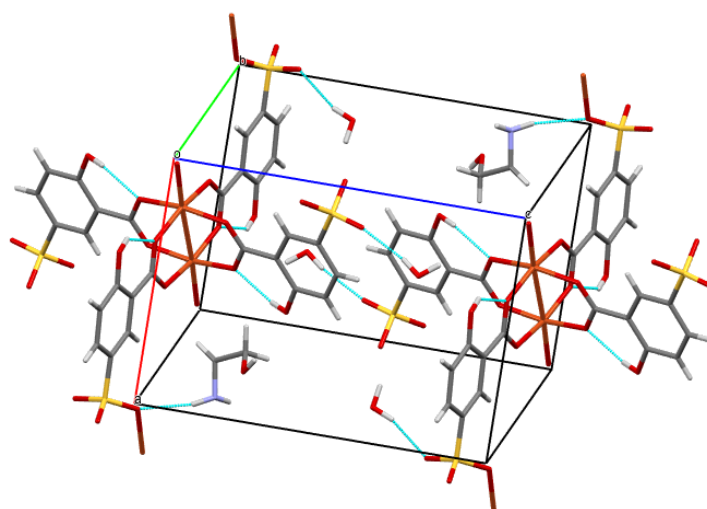


Figure 3. Crystal structure of the coordination polymer.

Impact Factor:	ISRA (India)	= 6.317	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
	ISI (Dubai, UAE)	= 1.582	ПИИЦ (Russia)	= 0.191	PIF (India)	= 1.940
	GIF (Australia)	= 0.564	ESJI (KZ)	= 8.100	IBI (India)	= 4.260
	JIF	= 1.500	SJIF (Morocco)	= 7.184	OAJI (USA)	= 0.350

Analysis of Hirshfeld surfaces of discrete coordination compound

Molecular crystalline structures can be quantitatively analyzed through the Hirshfeld surface technique. This methodology illuminates the shifts happening at every point on the Hirshfeld surface, pertaining to neighboring atoms situated on both the external and internal surfaces. These distinct attributes have been pivotal in scrutinizing the selectivity and specificity of intermolecular forces acting upon molecular arrangements.

The creation of these surfaces involves partitioning the space enclosed by the crystal using the Hirshfeld ratio, where the procrystal is effectively delineated by employing a promolecule characterized by an electron density of 0.5. The normalized contact distance, referred to as d_{norm} , is calculated by considering perspectives from both the exterior and interior of the surface, as outlined below:

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}}$$

The Hirshfeld surface analysis elucidates the intricate relationships between the external and internal components of a crystalline structure. The parameter denoted as d_{norm} represents the normalized contact distance, where d_e signifies the distance from the Hirshfeld surface to the nearest external nucleus, d_i denotes the corresponding distance to the nearest internal nucleus, and r^{vdW} designates the van der Waals radius of the atom in question.

The 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.

To analyze the short-range contacts between neighboring molecules in crystal lattice structures, the researchers utilized CrystalExplorer version 21.5 [15]. This software was employed to examine the Hirshfeld surfaces of the crystal structures and generate the corresponding two-dimensional (2D) fingerprint plots [16].

Hirshfeld analysis

Hirshfeld surface analysis was conducted on a coordination polymer complex using a CIF file. The asymmetric part of the structure was selected for the surface analysis, while the monoethanolamine and water molecules in the external sphere of the coordination complex were not considered. During the analysis, the Hirshfeld surface was derived from the normalized contact distance and its d_i and d_e indices.

Quantitative analysis of the Hirshfeld surface area (d_{norm}) revealed that the total volume is 453.59 Å³ and the surface area is 418.34 Å². Generally, larger volume and surface area indicate more extensive intermolecular bonding and interactions within the crystal structure.

The normalized bond distance, which provides a measure of atomic size, ranges from -0.6483 to 2.319 a.u. The parameter d_i , which represents the distance from the Hirshfeld surface to the nuclear state of the atoms inside and outside the surface, fell in the range from 0.9084 to 3.6866 a.u., while d_e ranged from 0.7751 to 3.4099 a.u. (Figure 4).

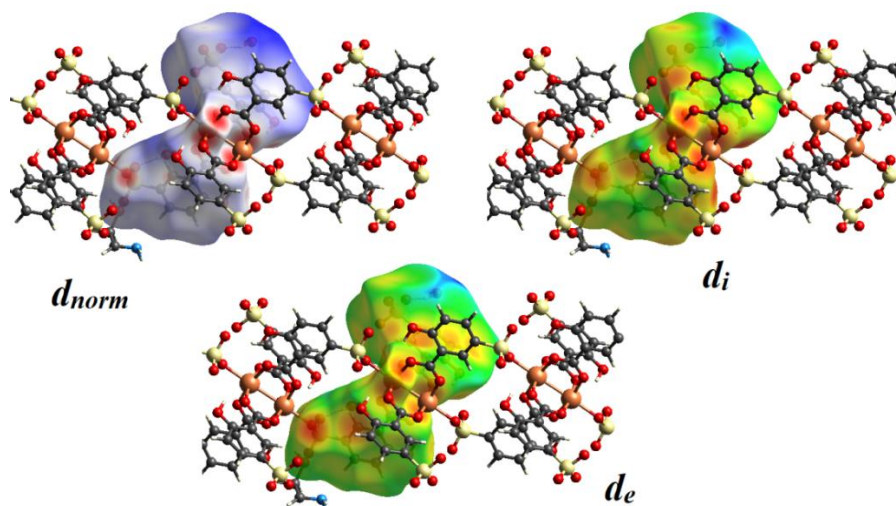


Figure 4. The appearance of the Hirshfeld surface found in d_{norm} , d_i , and d_e

The 2D fingerprints of the Hirshfeld surface of the polymer coordination compound are shown in Figure 5. Analysis of these fingerprint patterns

revealed five different homo- and heteroatomic contact interactions within and between molecules that contribute to the overall crystal packing.

Impact Factor:

ISRA (India) = 6.317
ISI (Dubai, UAE) = 1.582
GIF (Australia) = 0.564
JIF = 1.500

SIS (USA) = 0.912
ПИИИ (Russia) = 0.191
ESJI (KZ) = 8.100
SJIF (Morocco) = 7.184

ICV (Poland) = 6.630
PIF (India) = 1.940
IBI (India) = 4.260
OAJI (USA) = 0.350

The most prominent intermolecular interactions are H-O/O-H contacts, which account for 37.9 % of the Hirshfeld surface. The second largest contribution is H-H contacts, accounting for 19.1 % of the surface area. These close hydrogen-hydrogen interactions also play an important role in intermolecular packing. Other significant contributions include H-C/C-H contacts (13.9%) and O-O contacts (13.5%). These

reflect the various van der Waals and dipole-dipole interactions present in the crystal.

Slightly smaller proportions include Cu-O/O-Cu contacts (7.1%) and O-C/C-O contacts (6.5%), all of which also contribute to the Hirshfeld surface. This demonstrates the diverse molecular interactions that stabilize the crystal structure.

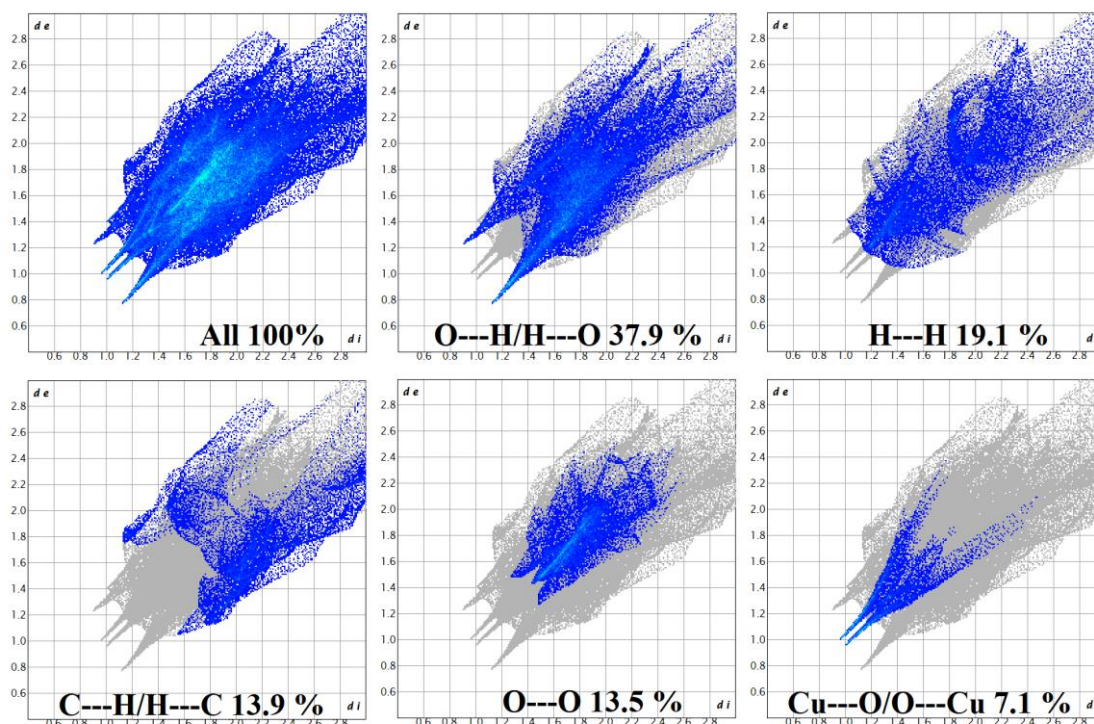


Figure 5. 2D representation of the Hirshfeld surface and the contributions of interatomic interactions to the formation of the surface.

According to Hirshfeld surface analysis, the contribution of similar elements to the overall surface formation inside and outside the molecular surface varies significantly, as shown in Table 3. Hydrogen contributes 31% to the internal surface and 59.7% to the external surface. Oxygen contributes 49% to the

internal surface and 29.5% to the external surface. Carbon contributes 15.9% to the internal surface and 6.1% to the external surface. Copper contributes 4.1% from the internal surface and 4% from the external surface.

Table 3. Contribution of atoms of the same element inside and outside the surface to the formation of the Hirshfeld surface and their differences.

	H	O	C	Cu
Inside	31	49	15.9	4.1
Outside	59.7	29.5	6.1	4

Conclusion

In conclusion, a novel coordination polymer (CP) with the formula $[\text{Cu}_2(\text{SSA})_4]_n(\text{MEA})_2(\text{H}_2\text{O})_4$ has been successfully synthesized and characterized. The compound exhibits a distinctive "paddle-wheel" or "Chinese lantern" structural motif, stabilized by both axial and equatorial coordination of sulphosalicylic acid (SSA) ligands to copper ions. Intramolecular

hydrogen bonding further enhances the stability of the structure. Hirshfeld surface analysis provides valuable insights into the intermolecular interactions within the crystal lattice. The analysis reveals the significant contributions of hydrogen and oxygen to both internal and external surfaces, while carbon and copper have relatively minor contributions. This study contributes to the growing field of coordination polymer

Impact Factor:	ISRA (India)	= 6.317	SIS (USA)	= 0.912	ICV (Poland)	= 6.630
	ISI (Dubai, UAE)	= 1.582	ПИИИ (Russia)	= 0.191	PIF (India)	= 1.940
	GIF (Australia)	= 0.564	ESJI (KZ)	= 8.100	IBI (India)	= 4.260
	JIF	= 1.500	SJIF (Morocco)	= 7.184	OAJI (USA)	= 0.350

chemistry, offering potential applications in areas such as catalysis, gas adsorption, and materials

science. Further investigations into the properties and potential applications of this novel CP are warranted.

References:

1. Fatima, A., Arora, H., Bhattacharya, P., Siddiqui, N., Abualnaja, K. M., Garg, P., & Javed, S. (2023). DFT, molecular docking, molecular dynamics simulation, MMGBSA calculation and hirshfeld surface analysis of 5-sulfosalicylic acid. *Journal of Molecular Structure*, 1273, 134242.
2. Liu, S., Dong, Y., Xu, L., & Kong, J. (2014). Effects of foliar applications of nitric oxide and salicylic acid on salt-induced changes in photosynthesis and antioxidative metabolism of cotton seedlings. *Plant Growth Regulation*, 73, 67-78.
3. Xue, J., Li, Z., Hao, W., Wang, X., Fan, G., Yu, L., & Geng, G. (2022). Effects of Soil Covering on Growth and Physio-Biochemical Indices of Sugar Beet Seedlings Under Short-Term Low-Temperature Stress. *Sugar Tech*, 24(5), 1530-1539.
4. Ezhilmathi, K., Singh, V. P., Arora, A., & Sairam, R. K. (2007). Effect of 5-sulfosalicylic acid on antioxidant activity in relation to vase life of Gladiolus cut flowers. *Plant Growth Regulation*, 51, 99-108.
5. Liu, Q., Du, K., Liu, M., Lv, R., Sun, B., Cao, D., ... & Wang, Z. (2019). Sulfosalicylic acid/Fe 3+ based nanoscale coordination polymers for effective cancer therapy by the Fenton reaction: an inspiration for understanding the role of aspirin in the prevention of cancer. *Biomaterials science*, 7(12), 5482-5491.
6. Purohit, P., Rawat, H., Verma, N., Mishra, S., Nautiyal, A., Bhatt, S., ... & Gupta, A. K. (2023). Analytical approach to assess anti-nutritional factors of grains and oilseeds: a comprehensive review. *Journal of Agriculture and Food Research*, 100877.
7. Fan, S. R., & Zhu, L. G. (2007). Structural diversity and fluorescent properties of copper (II) complexes constructed by 5-sulfosalicylate and 2, 2'-bipyridine. *Journal of molecular structure*, 827(1-3), 188-194.
8. Rehman, S. U., Islam, N., Ahad, S., Fatima, S. Z., & Pandith, A. H. (2013). Preparation and characterization of 5-sulphosalicylic acid doped tetraethoxysilane composite ion-exchange material by sol-gel method. *Journal of hazardous materials*, 260, 313-322.
9. Gupta, S., Fernandes, R., Patel, R., Spreitzer, M., & Patel, N. (2023). A review of cobalt-based catalysts for sustainable energy and environmental applications. *Applied Catalysis A: General*, 661, 119254.
10. Wang, W. G., Zhang, J., Song, L. J., & Ju, Z. F. (2004). Ferromagnetic linear trinuclear copper (II) complex bridged by sulfosalicylate ligand. *Inorganic Chemistry Communications*, 7(7), 858-860.
11. Smith, G., Wermuth, U. D., Young, D. J., & White, J. M. (2007). Polymeric structures in the metal complexes of 5-sulfosalicylic acid: The rubidium (I), caesium (I) and lead (II) analogues. *Polyhedron*, 26(14), 3645-3652.
12. Ibragimov, A. B., Ashurov, J. M., Ibragimov, B. T., Eshimbetov, A. G., Azimova, S. S., Tilyakov, Z. G., & Dusmatov, A. F. (2023). Synthesis, structure, Hirshfeld surface analysis of the new copper complex of 3, 5-dinitrobenzoic acid and docking study of its metal complexes bioactivity. *Journal of Molecular Structure*, 136105.
13. Groom, C. R., Bruno, I. J., Lightfoot, M. P., & Ward, S. C. (2016). The Cambridge structural database. *Structural Science*, 72(2), 171-179.
14. Ma, J. F., Yang, J., Li, L., Zheng, G. L., & Liu, J. F. (2003). The first ladder structure containing three different squares: the structure of barium 3-carboxy-4-hydroxybenzenesulfonate. *Inorganic Chemistry Communications*, 6(5), 581-583.
15. Ibragimov, A. B., Ashurov, J. M., Ibragimov, B. T., Eshimbetov, A. G., Azimova, S. S., Tilyakov, Z. G., & Dusmatov, A. F. (2023). Synthesis, structure, Hirshfeld surface analysis of the new copper complex of 3, 5-dinitrobenzoic acid and docking study of its metal complexes bioactivity. *Journal of Molecular Structure*, 136105.
16. Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D., & Spackman, M. A. (2021). CrystalExplorer: a program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *Journal of Applied Crystallography*, 54(3), 1006-1011.