HIRSHFELD SURFACE AND BOND VALENCE SUM (BVS) ANALYSES OF A TWO-DIMENSIONAL Pb(II)–M-SULFANILIC ACID COORDINATION POLYMER

Abdullaev Ahrorjon Khabibjonovich
PhD, Senior ResearcherInstitute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan,
100170, Mirzo Ulugbek str., 77a, Tashkent, Uzbekistan.
E-mail: ahrorabdullahabibjon@gmail.com
Ibragimov Aziz Bakhtiyarovich,
DSc, Professor, Director of the Institute Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan,
100170, Mirzo Ulugbek str., 77a, Tashkent, Uzbekistan.
E-mail: aziz_ibragimov@mail.ru

Abstract. Hirshfeld surface and bond valence sum (BVS) analyses were carried out to elucidate the nature of intermolecular interactions and the oxidation environment of Pb(II) ions in the two-dimensional Pb(II)–*m*-sulfanilic acid coordination polymer. The Hirshfeld surface analysis quantitatively revealed that O–H···O hydrogen bonds and Pb–O contacts play a crucial role in stabilizing the supramolecular framework, contributing 32.1% and 10.1% of the total surface contacts, respectively. The mapping of d_norm, shape index, and curvedness clearly identified regions of strong hydrogen bonding and π–π stacking interactions between aromatic rings. The bond valence sum (BVS) calculations confirmed the oxidation state of Pb(II) close to +2 (BVS = 1.87), indicating an accurate valence distribution consistent with the experimental crystallographic data. Together, the Hirshfeld and BVS analyses provide a comprehensive picture of the Pb(II) coordination environment, revealing how hydrogen bonding, lone-pair activity, and ligand geometry govern the structure and stability of the polymer.

Keywords: Hirshfeld surface analysis, BVS, Pb(II) coordination polymer, intermolecular interactions, supramolecular structure, crystal chemistry.

Annotatsiya. Ikki o‘lchovli Pb(II)–*m*-sulfanil kislotali koordinatsion polimerning molekulalararo o‘zaro ta’sirlari va Pb(II) ionining oksidlanish muhiti Hirshfeld sirt va bog‘ valentligi yig‘indisi (BVS) tahlillari yordamida o‘rganildi. Hirshfeld sirt tahlili O–H···O vodorod bog‘lari va Pb–O aloqalari supramolekulyar tuzilmani barqarorlashtirishda muhim rol o‘ynashini aniqladi; ular umumiy sirt kontaklarining mos ravishda 32,1% va 10,1% qismini tashkil etdi. d_norm, shape index va curvedness xaritalari aromatik halqalar orasidagi π–π o‘zaro ta’sirlar va kuchli vodorod bog‘lanish sohalarini aniq ko‘rsatdi. BVS hisob-kitoblari Pb(II) ionining oksidlanish darajasi +2 ga yaqin (BVS = 1,87) ekanini tasdiqladi. Ushbu tahlillar Pb(II) koordinatsion muhiti va supramolekulyar strukturaning barqarorligi

ISSN 3030-3907

ligand geometriyasi hamda Pb(II) ionining erkin juft elektron faoliyati bilan belgilanayotganini ko‘rsatadi.

Kalit so‘zlar: Hirshfeld sirt tahlili, BVS, Pb(II) koordinatsion polimeri, molekulalararo o‘zaro ta’sir, supramolekulyar tuzilma, kristall kimyo.

Аннотация. Анализ поверхности Хиршфельда и суммы валентных связей (BVS) был проведён для изучения природы межмолекулярных взаимодействий и состояния окисления ионов Pb(II) в двумерном координационном полимере Pb(II)–*m*-сульфаниловой кислоты. Анализ поверхности Хиршфельда показал, что водородные связи O–H···O и контакты Pb–O играют ключевую роль в стабилизации супрамолекулярного каркаса, составляя соответственно 32,1% и 10,1% от всех контактов поверхности. Карты d_norm, shape index и curvedness выявили области интенсивных водородных связей и π–π взаимодействий между ароматическими кольцами. Расчёты BVS подтвердили степень окисления Pb(II), близкую к +2 (BVS = 1,87), что согласуется с данными рентгеноструктурного анализа. В совокупности методы Хиршфельда и BVS дают полное представление о координационной среде Pb(II), показывая, как водородные связи, активность неподелённой пары и геометрия лиганда определяют структуру и устойчивость полимера.

Ключевые слова: анализ поверхности Хиршфельда, BVS, координационный полимер Pb(II), межмолекулярные взаимодействия, супрамолекулярная структура, кристаллохимия.

Introduction

In recent years, there has been increasing interest in the intentional synthesis of novel coordination polymers (CPs). These 2D MNS can be derived from bulk MOFs through appropriate chemical or physical exfoliation methods or can be directly synthesized with the aid of surfactants. They are expected to integrate the advantages of both MOFs and 2D materials [1–3]. Compared to conventional 3D MOFs, 2D MNS possess unique features such as ultrathin thickness, extensive specific surface areas, and increased accessibility to active sites, making them promising materials for a wide range of applications [4–6]. Two-dimensional coordination polymers (CPs) have demonstrated exceptional performance in the field of catalysis [7–10]. These structures are also known as two-dimensional metal–organic frameworks (2D MOFs) or two-dimensional metal–organic layers (MOLs) [11,12].]. In addition to the high surface activity typically associated with most 2D materials, CPs offer the unique benefit of specific and tunable chemical functionalities [13,14]. The design and synthesis of coordination polymers (CPs) have garnered significant interest from synthetic chemists. This is not only because CPs consist of networks formed by organic linkers and metal cations, often

ISSN 3030-3907

resulting in a wide variety of architectures and intriguing topologies, but also due to their potential industrial applications.

The existing literature indicates that coordination polymers of metanilic acid have been explored to a limited extent. In this article, we introduce a newly synthesized 2D coordination polymer made from lead (II) acetate and metanilic acid. A notable aspect of this compound's formation is the inclusion of a surfactant, resorcinol, which played a crucial role in guiding a distinctive polymerization process. As a result of this process, a 2D polymer was formed. Bond Valence Sum (BVS) analysis, Hirshfeld surface area, and other aspects of the compound have been thoroughly studied.

Hirshfeld surface analysis

Normalized contact distances between neighboring molecules in crystal lattice structures were calculated using Crystal Explorer version 21.5 [15]. Crystal Explorer 21.5 was employed to analyze Hirshfeld surfaces of crystal structures and generate corresponding two-dimensional (2D) fingerprint plots [16].

The asymmetric unit of the crystal structure was used for the analysis of the Hirshfeld surfaces of the coordination polymer compound. Figure 1 depicts the surface resulting from the calculation of normalized contact distances. The donor-acceptor bond regions of the central atom with the donor atom of the ligand are depicted in the main color gradient as large red regions. In some smaller red regions, the interaction regions of the hydrogen donor and acceptor, which ensure the formation of hydrogen bonds, are shown.

The d_{norm} Hirshfeld surface was formed at distances ranging from -0.4932 to 1.0398 atomic units, with a volume of 357.09 Å^3 and a surface area of 362.92 Å^2.

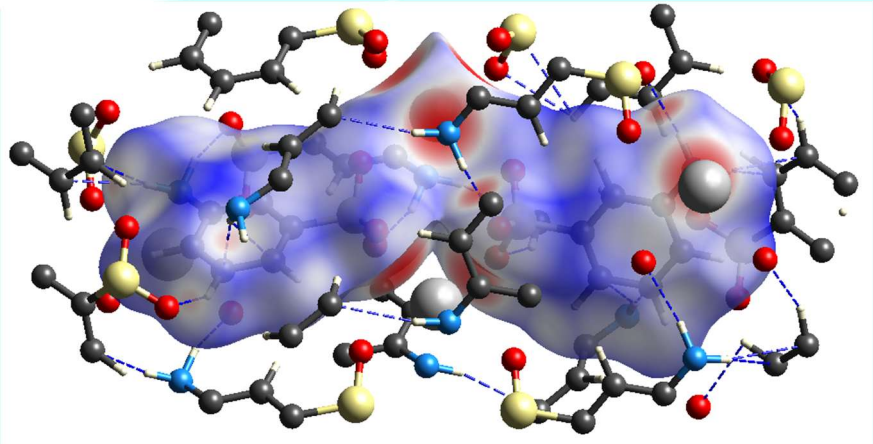


Figure 1. A d_{norm} representation of the Hirschfeld surface. Hirschfeld surface interactions with fragments up to 3.8 Å.

In the Hirshfeld surface analysis, the di, de, Shape Index, and Curvedness surfaces were also formed separately (Figure 2). The di, de, Shape Index, and Curvedness surfaces were displayed within the ranges of 0.9268 to 2.6098, 0.9318 to 2.4484, -1 to 1, and -4 to 4 atomic units, respectively. It was found that the minimum value

ISSN 3030-3907

of di is less than de (di <de), and the maximum value is greater than de (di > de), indicating that atoms at relatively long distances from the surface also contribute to its formation.

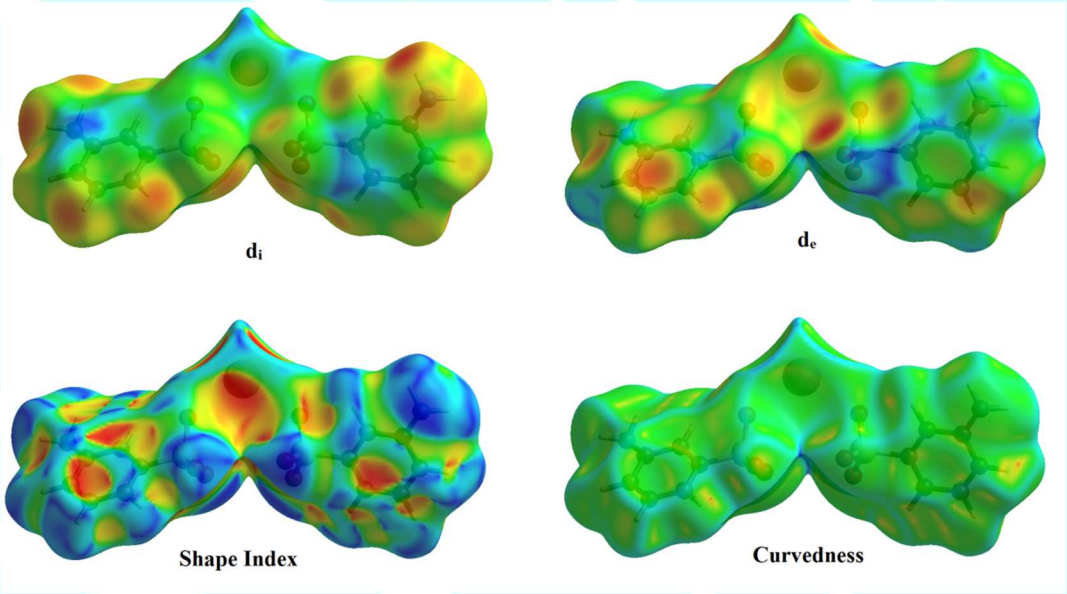


Figure 2. Hirshfeld surface di, de, shape index and curvature image, main boiling regions.

The contribution of molecules and interatomic interactions to the formation of the Hirshfeld surface varies, as illustrated in the 2D fingerprint image of the Hirshfeld surfaces of the compound (Fig. 3). The main contributions to the formation of the Hirshfeld surface of the coordination polymer compound are O---H/H---O interactions with 32.1%, H---H interactions with 24.8%, and C---H/H---C interactions with 16.7%. Pb---O/O---Pb interactions contribute 10.1%, and O---C/C---O interactions contribute 7.3%. Additionally, Pb---N/N---Pb, O---O, O---N/N---O, Pb---H/H---Pb, and Pb---C/C---Pb interactions contribute 4.3%, 2.6%, 0.9%, 0.7%, and 0.4% respectively to the Hirshfeld surface. Since these contributions are relatively small compared to the total surface, they occupy very little space in the 2D fingerprints.

ISSN 3030-3907

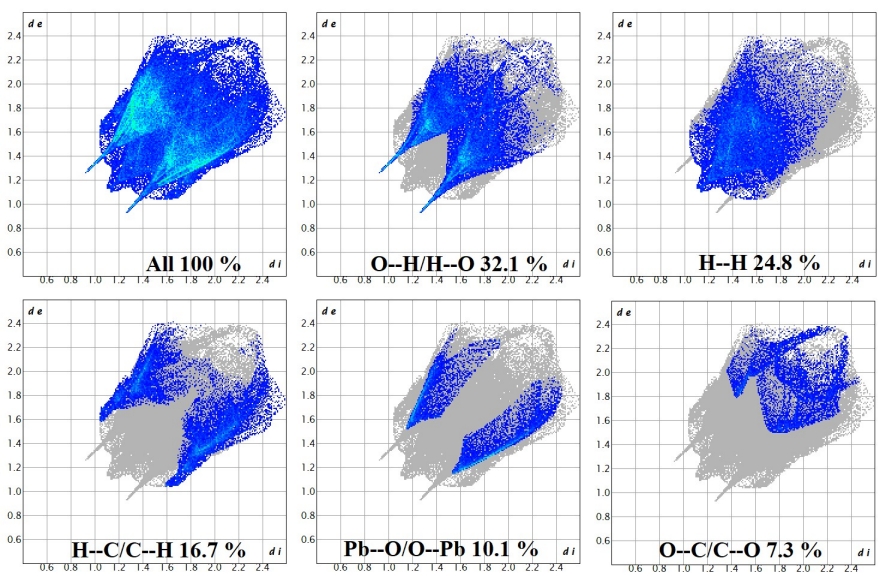
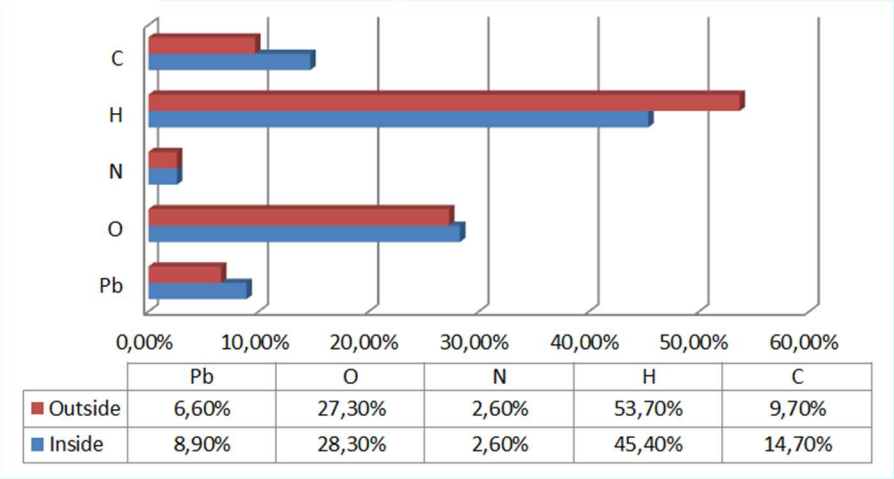


Figure 3. 2D fingerprint representation of a Hirshfeld surface showing the percentage contribution of interatomic interactions to surface formation

It was found that the contributions of atoms of the same element inside and outside the surface to the formation of the Hirshfeld surface are different (Fig. 4). The effects of carbon from similar elements inside and outside the surface are drastically different, whereas the contributions of hydrogen and oxygen to surface formation remain high both inside and outside the surface. Typically, in coordination compounds, the central atom does not contribute significantly to surface formation. However, in our study, we observe that the central atom, lead, contributes to surface formation both inside and outside the surface. This indicates the significant role of lead in the crystal formation of the polymer coordination compound.



	Pb	O	N	H	C
Outside	6,60%	27,30%	2,60%	53,70%	9,70%
Inside	8,90%	28,30%	2,60%	45,40%	14,70%

Figure 4. Hirschfeld surface formation contributions and differences of the same elements inside and outside the surface.

Bond Valence Sum Analysis

Bond valence sum (BVS) analysis is a method used to estimate the oxidation state of a central atom based on the lengths of the bonds it forms with its ligands

ISSN 3030-3907

[17]. In this study, the lead ion is coordinated by six oxygen atoms and two nitrogen atoms, creating a mixed coordination environment that suggests diverse bond strengths and lengths, contributing to the final BVS value [18,19]. The BVS for lead is calculated using the formula:

$$V = \sum v_{ij} = \sum exp\left(\frac{R_0 - R_{ij}}{b}\right)$$

Where V represents the bond valence sum, and v_{ij} is the bond valence of each Pb-X bond. R_0 is the bond valence parameter specific to the Pb-X bond [20] (X = O, with R_0 = 2.112 Å or N, with R_0 =2.18 Å) [21]. R_{ij} is the observed bond length, and b is a constant, typically 0.37 for Pb-O bonds and 0.40 for Pb-N bonds. The total BVS is the sum of the individual bond valences for all Pb-O and Pb-N bonds. In this complex, the individual contributions from the Pb-O and Pb-N bonds are summed to give a total BVS of 1.87 (Table 1). This value suggests that the lead ion is in an oxidation state close to +2, which is typical for lead in many complexes. The slight deviation from an integer value indicates minor distortions in the coordination geometry, possibly due to steric effects or electronic factors influencing the bond lengths. This analysis supports the conclusion that the lead complex has a predominantly covalent bonding character with some ionic contribution. The X-ray structure determined in this study is thus confirmed to be accurate.

Table 1.

Bond valance sum calculations of catena-(bis(μ3-3-aminobenzenesulfonato)-lead(II))

Co. No.	Bond distances (Å)								V = Σ v_{ij}
8	Pb(1)–O(1)	Pb(1)–O(2)	Pb(1)–O(3)	Pb(1)–O(4)	Pb(1)–O(5)	Pb(1)–O(6)	Pb(1)–N(1)	Pb(1)–N(2)	1.87*
	2.592(7)	2.773(7)	2.701(5)	2.560(7)	2.681(6)	2.781(7)	2.710(8)	2.687(8)	

Conclusion

A novel two-dimensional coordination polymer based on Pb(II) and *m*-sulfanilic acid has been successfully synthesized and structurally characterized. The crystal structure exhibits a hemidirected Pb(II) coordination geometry stabilized by extensive hydrogen bonding and sulfonate bridging. Hirshfeld surface analysis revealed that O–H/H–O and H–H contacts dominate the intermolecular interaction landscape, confirming the key role of hydrogen bonding in the supramolecular framework. Bond Valence Sum (BVS) analysis demonstrated that the Pb(II) ion retains an oxidation state close to +2, validating the structural integrity of the compound. Overall, this study provides a deeper understanding of

ISSN 3030-3907

Pb(II)-based coordination polymers and highlights the usefulness of combined Hirshfeld and BVS analyses in revealing intermolecular interactions and electronic structure contributions.

Acknowledgement

This research was carried out with the support of the *Institute of General and Inorganic Chemistry of the Uzbekistan Academy of Sciences*. The authors appreciate the institute's continuous encouragement and provision of research facilities.

REFERENCES

1. M. Zhao, Q. Lu, Q. Ma, H. Zhang, Two-Dimensional Metal–Organic Framework Nanosheets, Small Methods 1 (2017) 1600030. https://doi.org/10.1002/smtd.201600030.

2. C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G.-H. Nam, M. Sindoro, H. Zhang, Recent Advances in Ultrathin Two-Dimensional Nanomaterials, Chem. Rev. 117 (2017) 6225–6331. https://doi.org/10.1021/acs.chemrev.6b00558.

3. W. Xia, J. Li, T. Wang, L. Song, H. Guo, H. Gong, C. Jiang, B. Gao, J. He, The synergistic effect of Ceria and Co in N-doped leaf-like carbon nanosheets derived from a 2D MOF and their enhanced performance in the oxygen reduction reaction, Chem. Commun. 54 (2018) 1623–1626. https://doi.org/10.1039/C7CC09212A.

4. K. Zhao, S. Liu, G. Ye, Q. Gan, Z. Zhou, Z. He, High-yield bottom-up synthesis of 2D metal–organic frameworks and their derived ultrathin carbon nanosheets for energy storage, J. Mater. Chem. A 6 (2018) 2166–2175. https://doi.org/10.1039/C7TA06916B.

5. Z. Kang, L. Fan, D. Sun, Recent advances and challenges of metal–organic framework membranes for gas separation, J. Mater. Chem. A 5 (2017) 10073–10091. https://doi.org/10.1039/C7TA01142C.

6. Bétard, R.A. Fischer, Metal–Organic Framework Thin Films: From Fundamentals to Applications., Chem. Rev. 112 (2012) 1055–1083. https://doi.org/10.1021/cr200167v.

7. L. Tom, M.R.P. Kurup, A 2D-layered Cd(II) MOF as an efficient heterogeneous catalyst for the Knoevenagel reaction, Journal of Solid State Chemistry 294 (2021) 121846. https://doi.org/10.1016/j.jssc.2020.121846.

8. P. Li, W. Liu, J.S. Dennis, H.C. Zeng, Ultrafine Alloy Nanoparticles Converted from 2D Intercalated Coordination Polymers for Catalytic Application, Adv Funct Materials 26 (2016) 5658–5668. https://doi.org/10.1002/adfm.201601174.

9. A.M. Kirillov, Y.Y. Karabach, M.V. Kirillova, M. Haukka, A.J.L. Pombeiro, Topologically Unique 2D Heterometallic Cu II /Mg Coordination Polymer: Synthesis, Structural Features, and Catalytic Use in Alkane Hydrocarboxylation,

ISSN 3030-3907

Crystal Growth & Design 12 (2012) 1069–1074. https://doi.org/10.1021/cg201459k.
10. S. Zhou, G. Yan, B. Gao, W. Jiang, B. Liu, T. Zhou, C. Liu, G. Che, A layered Mn-based coordination polymer as an efficient heterogeneous catalyst for CO 2 cycloaddition under mild conditions, CrystEngComm 24 (2022) 4527–4533. https://doi.org/10.1039/D2CE00579D.
11. Dhakshinamoorthy, A.M. Asiri, H. Garcia, 2D Metal–Organic Frameworks as Multifunctional Materials in Heterogeneous Catalysis and Electro/Photocatalysis, Advanced Materials 31 (2019) 1900617. https://doi.org/10.1002/adma.201900617.
12. L. Cao, T. Wang, C. Wang, Synthetic Strategies for Constructing Two-Dimensional Metal-Organic Layers (MOLs): A Tutorial Review, Chin. J. Chem. 36 (2018) 754–764. https://doi.org/10.1002/cjoc.201800144.
13. M. Tran, K. Kline, Y. Qin, Y. Shen, M.D. Green, S. Tongay, 2D coordination polymers: Design guidelines and materials perspective, Applied Physics Reviews 6 (2019) 041311. https://doi.org/10.1063/1.5110895.
14. Y. Gong, T.J. Prior, C. Redshaw, Co/Mn-based 2D coordination polymers: synthesis, structure and ring opening polymerization, Inorganica Chimica Acta 561 (2024) 121871. https://doi.org/10.1016/j.ica.2023.121871.
15. Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. CrystalExplorer17.
16. Spackman, M. A.; Jayatilaka, D. Hirshfeld surface analysis. CrystEngComm 2009, 11, 19-32
17. HU, S.Z., XIE, Z.X. and Palenik, G., 2012. Bond Valence Parameters for Sn (II)—X and Sn (IV)—X (X= O, S, N, C, P, As, Se, Te, F, Cl, Br, I). Acta Physico-Chimica Sinica, 28(1), pp.19-24.
18. Brese, N.E. and O'keeffe, M., 1991. Bond-valence parameters for solids. Acta Crystallographica Section B: Structural Science, 47(2), pp.192-197.
19. Summers, S.P., Abboud, K.A., Farrah, S.R. and Palenik, G.J., 1994. Syntheses and structures of bismuth (III) complexes with nitrilotriacetic acid, ethylenediaminetetraacetic acid, and diethylenetriaminepentaacetic acid. Inorganic Chemistry, 33(1), pp.88-92.
20. Brown, I.D., 2016. The chemical bond in inorganic chemistry: the bond valence model (Vol. 27). Oxford university press.
21. Brown, I.D., 2000. The bond valence model as a tool for teaching inorganic chemistry: The ionic model revisited. Journal of Chemical Education, 77(8), p.1070.

ISSN 3030-3907