ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

STRUCTURAL AND SUPRAMOLECULAR INSIGHTS INTO A ONE-DIMENSIONAL POLY[SODIUM COBALT(II)–EDTA] COORDINATION POLYMER: A HIRSHFELD SURFACE STUDY

U.U.Ruziev
Department of Chemistry, Termez State University, 43 Barkamol Avlod Street, Termez-190111, Uzbekistan.
ruziyevumid86@gmail.com
Kh.Kh.Turaev
Department of Chemistry, Termez State University, 43 Barkamol Avlod Street, Termez-190111, Uzbekistan.
A.B. Ibragimov
Institute of General and Inorganic Chemistry, Uzbekistan Academy of Sciences M.Ulugbek Str., 77a, Tashkent 100170, Uzbekistan
Z.E.Djumayeva
Department of Chemistry, Termez State University, 43 Barkamol Avlod Street, Termez-190111, Uzbekistan.
G.Kh.Toirova
Department of Chemistry, Termez State University, 43 Barkamol Avlod Street, Termez-190111, Uzbekistan.
Kh.B.Kholturaev
Department of Chemistry, Termez State University, 43 Barkamol Avlod Street, Termez-190111, Uzbekistan.

Abstrac:

In this work, the crystalline structure and supramolecular structure of the poly[sodium cobalt (II) ethylene diaminetetraacetate aqua] complex were studied based on single-crystal X-ray diffraction and Hirschfeld surface analysis. The complex crystallizes in the monoclinic system, in the P_{21} space group, forming a one-dimensional coordination polymer structure. The Co (II) ion is coordinated in a deformed octahedral geometry through the donor set of the EDTA ligand N_2O_4. The sodium ion is located in a six-coordinate medium and ensures the formation of the polymer chain by binding neighboring Co-EDTA units. Analysis of the Hirschfeld surface showed that the main interactions determining the stability of the crystal lattice are O···H/H···O hydrogen bonds. In addition, the H···H, O···Na, and O···Co contacts contribute to the strengthening of the supramolecular structure. These results are

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

important for understanding the structural properties of bimetallic coordination polymers based on EDTA and for designing new functional materials.

Keywords: *Cobalt (II) complex; EDTA ligand; coordination polymer; sodium ions; crystalline structure; Hirschfeld surface analysis; hydrogen bonds*

Introduction

Coordination polymers (CPs) represent an important class of materials due to their diverse structural topologies, tunable chemical properties, and wide-ranging applications in catalysis, magnetism, gas storage, and molecular recognition [1–3]. Their modular nature, arising from the combination of metal ions and multifunctional ligands, enables the rational design of one-, two-, and three-dimensional frameworks with tailored functionalities [4]. In particular, the ability to form extended networks through bridging ligands makes CPs attractive for the development of functional materials [5–6].

Ethylenediaminetetraacetic acid (EDTA) is a versatile hexadentate ligand capable of coordinating to metal centers via two nitrogen and four carboxylate oxygen atoms [7–8]. Its rigid chelating framework not only stabilizes metal centers but also promotes the formation of extended coordination networks [Ref 9]. The presence of multiple donor sites and the possibility of additional hydrogen-bonding interactions render EDTA-based metal complexes suitable for constructing supramolecular architectures with high structural regularity [10–11].

Cobalt(II) ions are known for their flexible coordination geometries and ability to form stable octahedral complexes [12–13]. Previous studies on Co–EDTA complexes have reported discrete chelate units and, in some cases, polymeric structures; however, detailed investigations into their crystal structures, polyhedral geometries, and hydrogen-bonding networks remain limited [14–15]. Understanding these structural features is crucial for correlating coordination environments with the stability and functional properties of the resulting polymers [16].

In this work, we report the synthesis, single-crystal X-ray structural characterization, and comprehensive analysis of a novel one-dimensional Co–EDTA coordination polymer [17]. Detailed polyhedral and hydrogen-bonding analyses are presented, highlighting the role of the Co(II) centers, sodium ions, and coordinated water molecules in stabilizing the framework. This study provides insights into the coordination behavior, supramolecular interactions, and structural regularity of EDTA-based cobalt polymers, thereby contributing to the rational design of metal–ligand polymeric materials [18].

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

Synthesis of the complex

Ethylenediaminetetraacetic acid (EDTA, 0.744 g, 0.10 M) was dissolved in distilled water under continuous stirring, and the pH was adjusted to 7.0–8.0 using 0.10 M NaOH. For the synthesis of complex (1), 20 mL of distilled water served as the solvent. To the ligand solution, 10.0 mL of 0.10 M 4-nitroaniline was added as a catalyst, and the mixture was stirred magnetically at 600 rpm for 1 h at 25 ± 1°C until a clear solution was obtained. $Co(NO_3)_2 \cdot 6H_2O$ (0.582 g, 0.10 M), dissolved in 20 mL of distilled water, was then added dropwise, followed by ultrasonic treatment for 10–15 min to ensure thorough homogenization. The resulting solution was kept at 40–45°C to allow slow evaporation, leading to the formation of dark-green, cubic-shaped crystals of complex (1) over 10 days, with an isolated yield of 78%.

Crystal structure

The crystal structures of Poly[sodium cobalt(II) ethylenediaminetetraacetate aqua] (1) reveal distinct one-dimensional coordination frameworks influenced by the crystallization solvent. Complex (1), crystallized from an aqueous medium, belongs to the monoclinic crystal system and adopts a noncentrosymmetric space group P21 with Z = 2 (Table 1.).

The asymmetric unit of complex (1) comprises one complete EDTA ligand coordinated to a Co(II) ion, along with a sodium ion (Na(1)) and a coordinated water molecule [O(6), O(7)] (Fig. 2(a)). The Co(II) center adopts an octahedral geometry defined by two nitrogen atoms and four carboxylate oxygen atoms from the

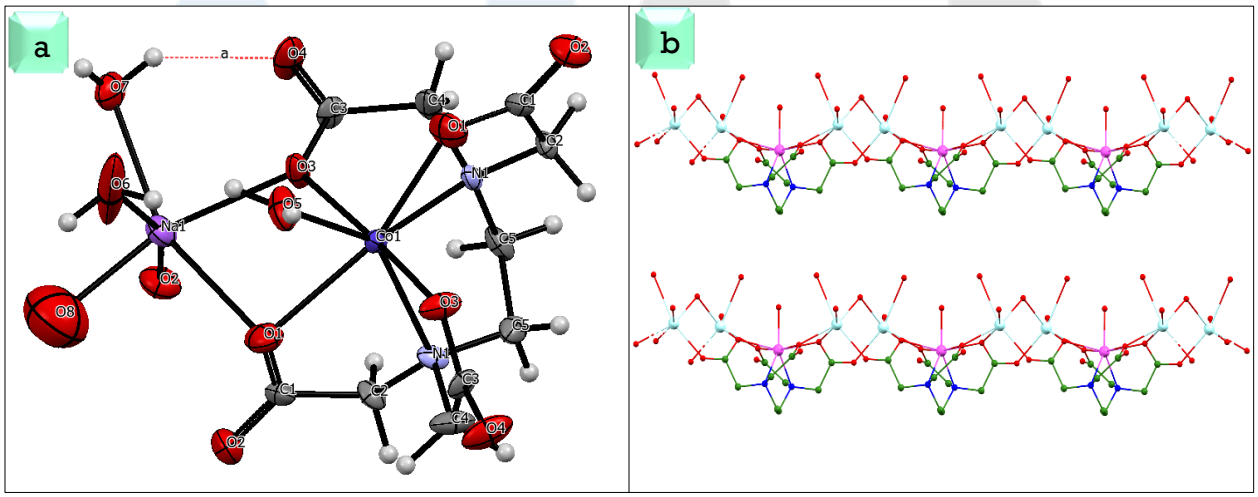

Figure 1. (a) Asymmetric unit of Poly[sodium cobalt(II) ethylenediaminetetraacetate aqua] showing the Co(II) center with EDTA, Na^+, and coordinated water; (b) one-dimensional polymeric chain with Co(II) centers connected via EDTA and Na^+ ions.

hexadentate EDTA ligand, forming a stable Co-EDTA chelate unit. The sodium ion bridges carboxylate oxygen atoms of the EDTA ligand and the coordinated water

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

molecule (O9), generating an extended coordination network. These Na-O linkages, together with O-H···O hydrogen-bonding interactions, further stabilize the one-dimensional supramolecular framework.

Complex (1) forms a one-dimensional coordination polymer (Fig. 1), in which the Co(II) center is chelated by the EDTA ligand through two nitrogen and four oxygen donor atoms, resulting in a slightly distorted octahedral geometry (Fig. 2). The Co atom is coordinated by four carboxylate oxygen atoms of the EDTA ligand, with an average Co-O bond length of 2.056(3) Å, and by two nitrogen atoms from the ethylenediamine moiety, with an average Co-N bond length of 2.2058(3) Å. The mean Co-donor distance of 2.2146 Å falls within the typical range reported for octahedral Co(II) complexes. Polyhedral analysis yields a polyhedral volume of 15.8918 Å^3 and a distortion index of 0.04220, indicating a modest deviation from ideal octahedral geometry, primarily arising from chelate-induced strain and ligand-metal electronic effects.

In the crystal structure, a single crystallographically independent sodium ion, Na(1), is present and exhibits a six-coordinate environment that plays a key role in the construction of the supramolecular framework. The Na(1) ion adopts a distorted octahedral coordination geometry defined by six oxygen donor atoms, four originating from the carboxylate groups of the EDTA ligand and two from a coordinated water molecule (O5). The equatorial plane of the coordination polyhedron is formed by three carboxylate oxygen, two aqua oxygen atoms, resulting in a slightly distorted octahedral arrangement. The Na-O bond lengths span the range 2.264(13)-2.691(12) Å, with an average distance of 2.4238 Å. Polyhedral analysis yields a coordination polyhedron volume of 17.4375 Å^3 and a distortion index of 0.05034, indicative of moderate deviation from ideal octahedral geometry. The effective coordination number (ECoN = 5.2242) further supports the presence of a slightly distorted six-coordinate environment around the Na(1) center. This coordination configuration enables the Na(1) ion to act as a bridging node, linking adjacent Co-EDTA coordination units through shared oxygen atoms and thereby extending the structure into a one-dimensional polymeric chain. In addition, the coordinated water molecule (O9) participates in hydrogen-bonding interactions with neighboring acceptor atoms, contributing significantly to the stabilization of the crystal lattice.

The crystal structure of the Co-EDTA complex is stabilized by an extensive hydrogen-bonding network involving both coordinated and lattice water molecules, as well as oxygen atoms from the EDTA ligand. As summarized in Table 2, several O-H···O hydrogen bonds with donor-acceptor distances ranging from 2.734(12) to

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

2.872(12) Å are observed, indicating moderate to relatively strong hydrogen-bonding interactions. In particular, the O(5)-H(5A)···O(6) and O(5)-H(5B)···O(6) interactions display identical donor-acceptor distances of 2.734 Å but differ in their H···A separations and bond angles, suggesting asymmetric bifurcated hydrogen bonding involving water molecules. Similarly, the O(6)-H(6A)···O(5) and O(6)-H(6B)···O(4) hydrogen bonds further interlink adjacent coordination units, contributing to the formation of a three-dimensional supramolecular network. The relatively large D-H···A angles, particularly for O(5)-H(5B)···O(6) (158°) and O(7)-H(7B)···O(2) (162°), indicate directionally favorable hydrogen bonds, which play a significant role in reinforcing the crystal packing. In addition to classical O-H···O hydrogen bonds, weak C-H···O interactions are also present, such as C(2)-H(2B)···O(7) and C(4)-H(4A)···O(1), with donor-acceptor distances of 3.453(8) and 3.527(10) Å, respectively. Although weaker in nature, these interactions further stabilize the crystal lattice by linking neighboring molecules and filling voids within the structure.

Table 2. Hydrogen bond for poly[NaCo(EDTA)(H_2O)]

D-H•••A	d(D-H)	d(H•••A)	d(D•••A)	<(DHA)
O(5)-H(5A)•••O(6)	0.8500	2.2200	2.734(13)	119.00
O(5)-H(5B)•••O(6)	0.8500	1.9300	2.734(12)	158.00.
O(6)-H(6A)•••O(5)	0.8900	2.0200	2.734(12)	136.00.
O(6)-H(6B)•••O(4)	0.9000	2.0700	2.872(12)	149.00
O(7)-H(7A)•••O(4)	0.8600	2.1200	2.846(8)	142.00.
O(7)-H(7B)•••O(2)	0.8600	2.0300	2.860(8)	162.00
C(2)-H(2B)•••O(7)	0.9700	2.5100	3.453(8)	163.00
C(4)-H(4A)•••O(1)	0.9700	2.5800	3.527(10)	165.00

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

CrystalData	
Formula	C5H11Co0.5NNaO7
FormulaWeight	249.60
CrystalSystem	monoclinic
Spacegroup	C2(No.5)
a,b,c[Å]	11.4372(7),9.7601(4),8.8638(5)
α,β,γ[°]	90,111.069(7),90
V[Å^3]	923.30(10)
Z	4
D(calc)[g/cm^3]	1.796
Mu(CuKa)[mm^{-1}]	8.490
F(000)	514
CrystalSize[mm]	0.05x0.30x0.30
DataCollection	
Temperature(K)	293
Radiation[Å]	CuKa1.54184
ThetaMin-Max[°]	5.3,75.9
Dataset	-14≤11;-10≤12;-7≤10
Tot.,Uniq.Data,R(int)	1665,1212,0.041
ObservedData[I>0.0sigma(I)]	1199
Refinement	
Nref,Npar	1212,139
R,wR2,S	0.0545,0.1460,1.04
Max.andAv.Shift/Error	0.00,0.00
Min.andMax.Resd.Dens.[e/Å^3]	-0.55,0.76
CCDC	**2515362**

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

Table1. Crystal data and detail of the structure determination for

Table 3. Polyhedral parameters for compound (1).

Bond	**Distance (Å)**	**Bond**	**Distance (Å)**
Na(1)-O(8)	2.264(13)	Co(1)-O(5)	2.093(7)
Na(1)-O(3)	2.320(7)	Co(1)-O(3)	2.112(4)
Na(1)-O(2)	2.364(7)	Co(1)-O(3)	2.112(4)
Na(1)-O(7)	2.381(7)	Co(1)-N(1)	2.237(6)
Na(1)-O(1)	2.522(6)	Co(1)-N(1)	2.237(6)
Na(1)-O(6)	2.691(12)	Co(1)-O(1)	2.356(7)
-	-	Co(1)-O(1)	2.356(7)
Average bond length (Å)	2.4238		2.2146
Polyhedral volume ($Å^3$)	17.4375		15.8918
Distortion index (bond length)	0.05034		0.04220
Quadratic elongation	1.0620		-
Bond angle variance ($deg.^2$)	186.4908		-
Effective coordination number	5.2242		6.3373

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

In this work, intermolecular interactions in the crystalline structure of a one-dimensional (1D) polymer complex consisting of EDTA ligand, cobalt (II) and sodium cations, and crystallization water molecules were studied using Hirschfeld surface analysis. This approach allows for a qualitative and quantitative assessment of the nature of intermolecular contacts in the crystal lattice and their relative proportions.[Ref 19] Figure 3 shows the Hirschfeld surface maps calculated for the complex, which are represented in the form of dnorm, de, di, and the shape index. The red areas observed on the dnorm surface indicate the presence of short-distance and strong intermolecular contacts. These red spots mainly correspond to hydrogen bonds of the O···H/H···O type and reflect the interactions between the carboxylate oxygen atoms in the EDTA ligand and water molecules and uncoordinated hydrogen atoms. de (external distance) and di (internal distance) maps allow for a separate assessment of the distances from the atoms inside the molecule to the surface. With the help of these maps, the coordination medium formed by oxygen atoms around the cobalt and sodium centers, as well as continuous bonds along the polymer chain, are clearly visible. The shape index map represents the surface compatibility between adjacent fragments, showing that the spatial arrangement of molecules in the crystal lattice is closely coordinated with each other.

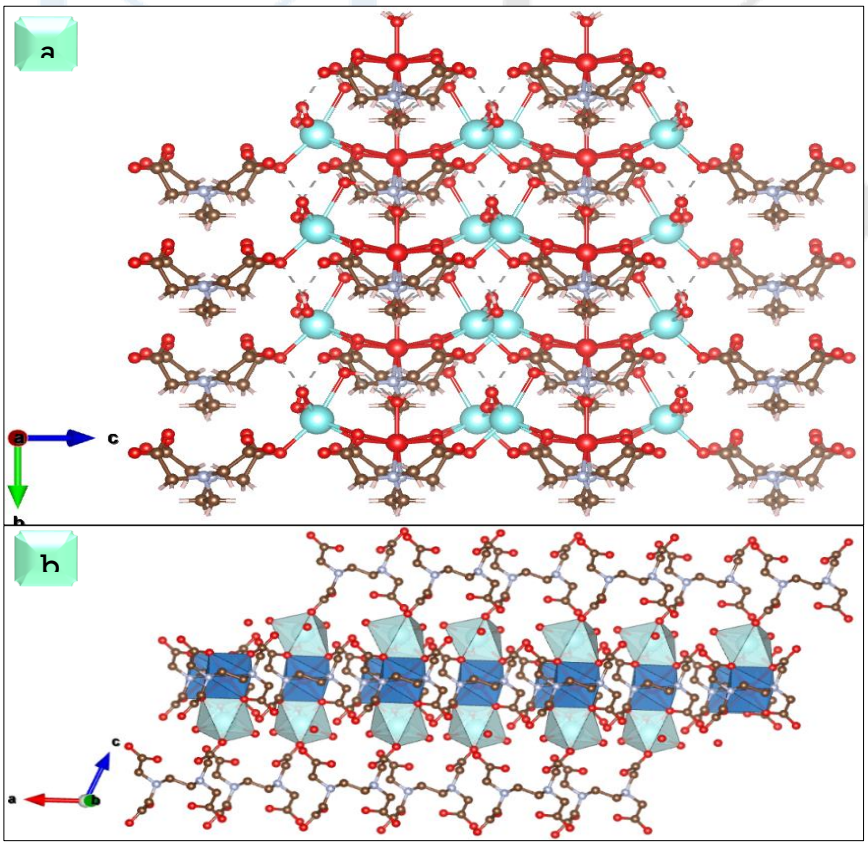

Figure 2. (a) One-dimensional poly[sodium cobalt(II) ethylenediaminetetraacetate aqua] polymeric chain; (b) Co(II) polyhedral octahedron.

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

This shows the strong and directed network of hydrogen bonds formed with the participation of carboxylate oxygen atoms and crystallization water molecules in the EDTA ligand. These contacts are the main stabilizing factor of the complex crystal lattice. H···H contacts - 32.8%. This significant contribution confirms that molecules are densely packed within the crystalline structure and that Van der Waals type interactions play an important role. O···Na/Na···O contacts - 10.6%. Electrostatic and coordination interactions of sodium cations with carboxylate groups and water molecules ensure structural integrity along the 1D polymer chain. O···Co/Co···O contacts constitute 3.1%. Coordination bonds formed by oxygen donor atoms around the cobalt (II) center strengthen the one-dimensional structure of the polymer complex. The remaining small fractions correspond to secondary contacts, such as C···H and C···O, which contribute to the strengthening of the overall crystal structure.

Analysis of Hirschfeld's surface showed that hydrogen bonds and metal-ligand interactions are important in the crystalline structure of the 1D polymer complex based on dimensional poly[sodium cobalt(II) ethylenediaminetetraacetate aqua]. In particular, the predominance of O···H/H···O contacts proves that the stability of the crystal lattice is ensured by a network of three-dimensional hydrogen bonds formed by water molecules and carboxylate groups. These results will serve as an important scientific basis for a deeper understanding of the structural features of this complex and the design of similar polymer complexes in the future.

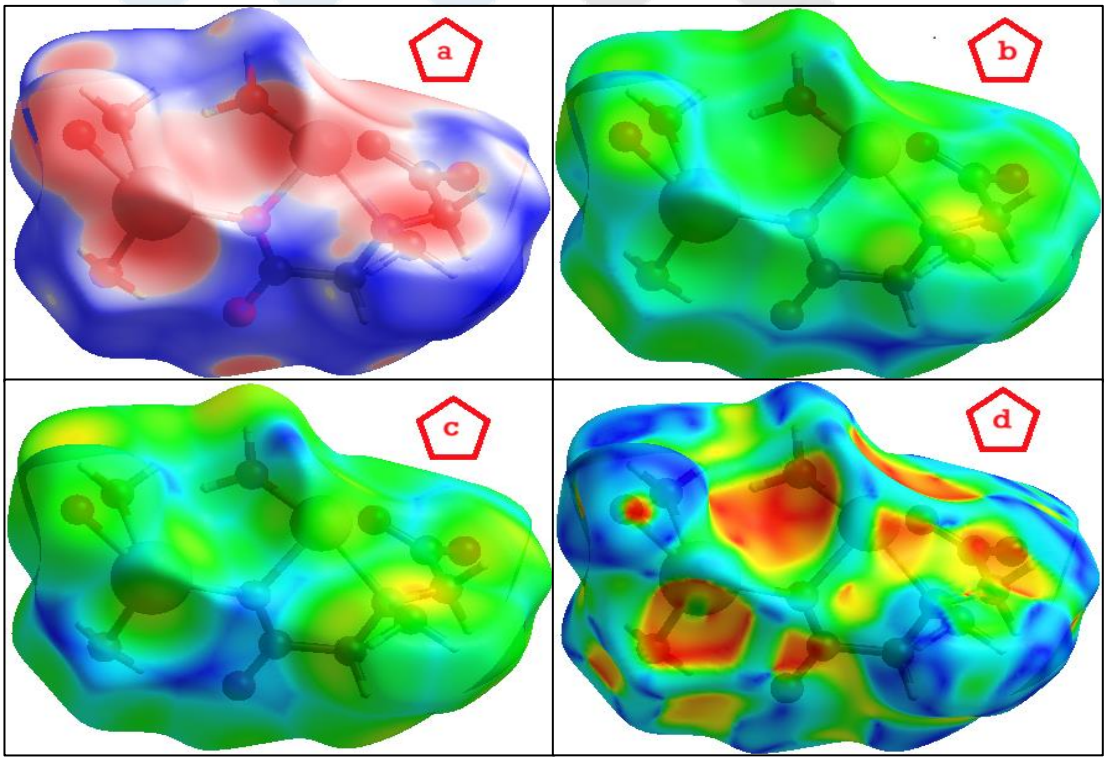

Figure 3. Hirshfeld surface maps: (a) d_{norm}, (b) d_e, (c) d_i, (d) shape index.

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889,
2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

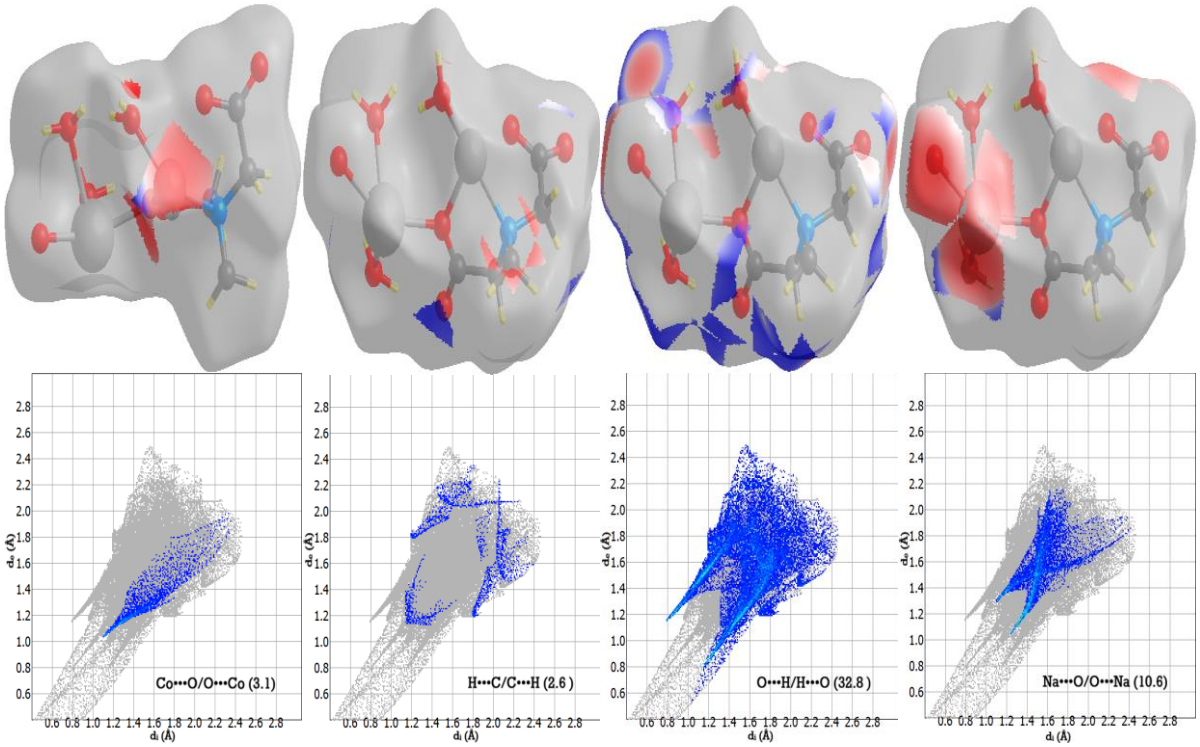

Figure 4. Fingerprint plots and d_{norm} Hirshfeld surface

Conclusion

These results reveal the structural properties of bimetallic coordination polymers based on EDTA. In this work, the crystalline and supramolecular structure of the poly[sodium cobalt (II) ethylene diaminetetraacetate aqua] complex was studied in depth and systematically. The results of X-ray structural analysis clearly showed that the Co (II) center forms a stable, slightly deformed octahedral coordination medium with the EDTA ligand, and the Na (I) ion forms a one-dimensional coordination polymer chain by binding adjacent Co-EDTA fragments through carboxylate oxygen atoms and water molecules. Polyhedral analysis confirms a moderate deviation of the coordination medium around Co (II) and Na (I) from the ideal geometry, which is explained by chelate effects and ion-ligand interactions and the design of new functional materials. Analysis of Hirschfeld's surface quantitatively and qualitatively revealed the nature of interactions in the crystal lattice and proved that hydrogen bonds of the O···H/H···O type are the main stabilizing factor of the crystal structure. In addition, the significant contribution of H···H, O···Na, and O···Co contacts indicates the co-operation of coordination and electrostatic interactions, ensuring the structural integrity of the polymer chain. As a result of the synergistic interaction of the metal-ligand coordination and the three-dimensional hydrogen bond network, a strong supramolecular architecture is formed. The obtained results make a significant

contribution to a deeper understanding of the structure-property relationships of metal-organic coordination polymers based on EDTA and expand the prospects for the targeted design of such systems and their use as functional materials. This research will serve as a reliable scientific basis for the further synthesis of polymer complexes with the participation of alkali metal ions and the regulation of their structural diversity.

References:

1. Alexandrov E. V. et al. Topological methods for analysis and design of coordination polymers //Russian chemical reviews. – 2022. – Т. 91. – №. 4. – С. RCR5032.
2. Shakeel R. et al. Multifunctional nanomaterials in materials chemistry: A cross-disciplinary review of applications in energy, environment, catalysis, and biomedicine //Scholars Journal of Engineering and Technology. – 2025. – Т. 8. – С. 673-707.
3. Sundaram G. A. et al. Introduction and advancements in room-temperature ferromagnetic metal oxide semiconductors for enhanced photocatalytic performance //ChemEngineering. – 2024. – Т. 8. – №. 2. – С. 36.
4. Haldar R., Maji T. K. Metal–organic frameworks (MOFs) based on mixed linker systems: structural diversities towards functional materials //CrystEngComm. – 2013. – Т. 15. – №. 45. – С. 9276-9295.
5. Zheng N. et al. Dynamic covalent polymer networks: a molecular platform for designing functions beyond chemical recycling and self-healing //Chemical Reviews. – 2021. – Т. 121. – №. 3. – С. 1716-1745.
6. Wang X., McHale R. Metal-containing polymers: building blocks for functional (nano) materials //Macromolecular rapid communications. – 2010. – Т. 31. – №. 4. – С. 331-350.
7. Zhang K. et al. EDTA-based adsorbents for the removal of metal ions in wastewater //Coordination Chemistry Reviews. – 2021. – Т. 434. – С. 213809.
8. Douglas B. E., Radanović D. J. Coordination chemistry of hexadentate EDTA-type ligands with M (III) ions //Coordination chemistry reviews. – 1993. – Т. 128. – №. 1-2. – С. 139-165.
9. He T., Kong X. J., Li J. R. Chemically stable metal–organic frameworks: rational construction and application expansion //Accounts of chemical research. – 2021. – Т. 54. – №. 15. – С. 3083-3094.
10. Teixeira J. M. C. Paramagnetic NMR of Proteins to study the Collagenolytic Mechanism of MMP-1 : дис. – Universidade de Coimbra (Portugal), 2013.

ISSN: 2582-4686 SJIF 2021-3.261,SJIF 2022-2.889, 2024-6.875 ResearchBib IF: 9.948 / 2024

THE MULTIDISCIPLINARY JOURNAL OF SCIENCE AND TECHNOLOGY

VOLUME-5, ISSUE-12

11. Subirana J. A., Soler-Lopez M. Cations as hydrogen bond donors: a view of electrostatic interactions in DNA //Annual review of biophysics and biomolecular structure. – 2003. – Т. 32. – №. 1. – С. 27-45.
12. Wang X. et al. Multifunctional cobalt (II) coordination polymers tuned by flexible bis (pyridylamide) ligands with different spacers and polycarboxylates //Crystal growth & design. – 2014. – Т. 14. – №. 7. – С. 3438-3452.
13. Long T. et al. Incorporating highly anisotropic four-coordinate Co (II) ions within one-dimensional coordination chains //Crystal Growth & Design. – 2023. – Т. 23. – №. 4. – С. 2980-2987.
14. Mudsainiyan R. K., Chawla S. K. Synthesis, characterizations, crystal structure determination of μ6 coordinated complex of Co (III) with EDTA and its thermal properties //Molecular Crystals and Liquid Crystals. – 2015. – Т. 606. – №. 1. – С. 237-245.
15. Mudsainiyan R. K., Jassal A. K., Chawla S. K. New water soluble heterometallic complex showing unpredicted coordination modes of EDTA //Journal of Solid State Chemistry. – 2015. – Т. 230. – С. 61-69.
16. Jung J. H. et al. Coordination polymer gels with important environmental and biological applications //Chemical Society Reviews. – 2013. – Т. 42. – №. 3. – С. 924-936.
17. Ghanbari B. et al. Synthesis, X-ray crystallography, thermogravimetric analysis and spectroscopic characterization of isostructural one-dimensional coordination polymers as sorbents for some anions //CrystEngComm. – 2018. – Т. 20. – №. 13. – С. 1783-1796.
18. Saini H. et al. Hierarchical porous metal–organic framework materials for efficient oil–water separation //Journal of Materials Chemistry A. – 2022. – Т. 10. – №. 6. – С. 2751-2785.
19. Gavezzotti A. Towards a realistic model for the quantitative evaluation of intermolecular potentials and for the rationalization of organic crystal structures. Part I. Philosophy //CrystEngComm. – 2003. – Т. 5. – №. 76. – С. 429-438.
20. Suyunov J. R. et al. Synthesis, crystal structure and Hirshfeld surface analysis of diaquabis (o-phenylenediamine-κ2N, N′) nickel (II) naphthalene-1, 5-disulfonate //Structure Reports. – 2023. – Т. 79. – №. 11. – С. 1083-1087.