SOLVOTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF THE MANGANESE(II) COORDINATION POLYMER $[Mn_2(Br_2BDC)_2(DMF)_3]_n$

MORPHOLOGY

Tursunov B.Ch[1], Muxammadaliyev X.G'[1], Ibroximov J.A[1]

[1]Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, 77a Mirzo Ulugbek Street, 100170 Tashkent, Uzbekistan

e-mail: tursunovbakhtiyor744@gmail.com ORCID:https://orcid.org/0009-0005-0346-4251

INTRODUCTION

Coordination polymers and metal-organic frameworks form when metal ions combine with organic bridging ligands to give infinite one-, two- or three-dimensional crystalline structures. The scientific importance of this field was recognized in 2025 by the award of the Nobel Prize in Chemistry to S. Kitagawa, R. Robson and O. M. Yaghi [1]. In recent years, coordination polymers of Ni(II), Cu(II), Cd(II) and other metals based on carboxylate ligands have been synthesized, and their crystal structures and functional properties have been studied in detail [2], [3]. Manganese(II)-based systems are of particular interest because the high-spin d^5 configuration allows the coordination sphere to adopt a variety of geometries. A two-dimensional Mn(II) coordination polymer with 2,5-dibromoterephthalate was obtained by the solvothermal method, and its dielectric properties and surface area were characterized [4]; for a Cd(II) polymer based on isonicotinate, structural and textural data were analyzed together [5]. Nevertheless, the synthesis and crystal structure of compounds in the Mn(II)-2,5-dibromoterephthalate-DMF system remain insufficiently studied. The aim of this work is to synthesize a new coordination polymer of composition $[Mn_2(Br_2BDC)_2(DMF)_3]_n$ (Br_2BDC^{2-} = 2,5-dibromoterephthalate, DMF = N,N-dimethylformamide) by the solvothermal method and to determine its crystal structure.

SYNTHESIS METHOD

$MnCl_2 \cdot 4H_2O$, 2,5-dibromoterephthalic acid (H_2Br_2BDC) and N,N-dimethylformamide, each of at least 98% purity, were used without further purification. The Mn(II) salt (20.0 mmol) and H_2Br_2BDC (10.0 mmol) were dissolved in 10 mL of DMF; the mixture was placed in a Teflon-lined steel autoclave, heated at 120 °C for 48 h, and cooled to room temperature at a rate of 30 °C/h. The resulting colorless or pale yellow crystals were filtered off, washed with water and dried in air; the yield based on Mn was 65%. Slow cooling allowed the growth of crystals suitable for single-crystal X-ray diffraction analysis. In this process, DMF serves as the reaction medium and also acts as a ligand coordinated to the metal center.

Crystal structure. The structure was determined by single-crystal X-ray diffraction analysis: the crystal is tetragonal, space group $I4_1/a$, $a = b = 38.9316(4)$ Å, $c = 8.9272(2)$ Å, $V = 13530.7(4)$ Å^3, $Z = 16$; the refinement indicator is $R_1 = 0.0437$ ($I > 2\sigma(I)$). Calculations were performed with SHELXT, SHELXL and Olex2. The asymmetric unit contains two crystallographically independent Mn(II) centers, which are linked through a common bridging O(11) atom to form a dinuclear fragment. Mn(2) is surrounded by six oxygen atoms; the Mn-O distances range from 2.106(3) to 2.411(3) Å, with a mean value of 2.215 Å and a distortion index of 0.047. The O(2) and O(3) atoms around Mn(1) are disordered over two positions (A/B); the mean Mn-O distances for the A and B conformers are 2.191 and 2.147 Å, respectively. These values are typical of high-spin six-coordinate Mn^{2+} and confirm the +2 oxidation state of manganese.

The projection of the crystal structure along the *c* axis is shown in Fig. 1. The Mn(1) and Mn(2) polyhedra are arranged in pairs and form dinuclear blocks; these blocks are connected by 2,5-dibromoterephthalate ligands into a regular lattice in the *a* and *b* directions. The DMF molecules are coordinated to the Mn centers as terminal ligands, and the bromine atoms are located at the edges of the ligand rings, pointing

into the voids between the polyhedra. Because strong hydrogen-bond donors are absent, the crystal packing is stabilized by four weak C-H···O hydrogen bonds (*D*···*A* 3.06-3.40 Å) and van der Waals interactions.

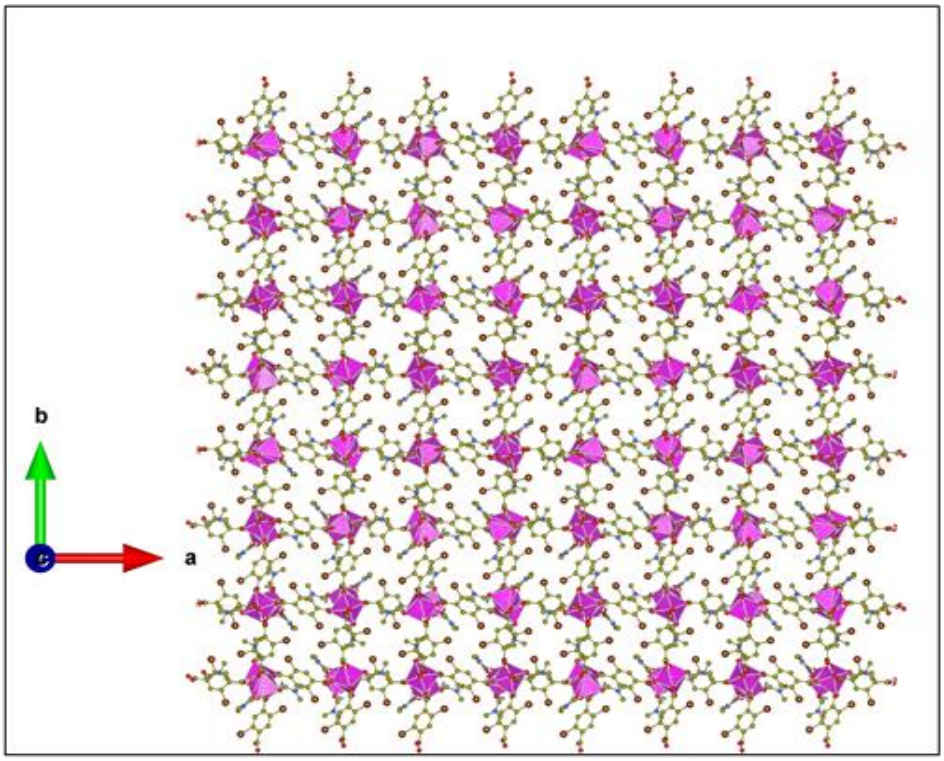


Fig. 1. Projection of the crystal structure of $[Mn_2(Br_2BDC)_2(DMF)_3]_n$ along the *c* axis (Mn polyhedra - pink-violet, Br - brown, O - red, N - blue, C - gold).

CONCLUSION

The new Mn(II) coordination polymer of composition $[Mn_2(Br_2BDC)_2(DMF)_3]_n$ was synthesized from $MnCl_2 \cdot 4H_2O$ and 2,5-dibromoterephthalic acid in DMF by the solvothermal method (120 °C, 48 h), with a yield of 65%. Single-crystal X-ray diffraction analysis showed that two independent Mn(II) centers in the structure form a dinuclear fragment through a common bridging O(11) atom; the Mn-O distances (mean 2.147-2.215 Å) are consistent with high-spin Mn(II).

REFERENCES

1. The Nobel Prize in Chemistry 2025. NobelPrize.org,

2025.https://www.nobelprize.org/prizes/chemistry/2025/summary/

2. Ruziev, U. U. U., Turaev, K. K., Kholturaev, K. B. U., Saidov, D. K. U., Adinaev, K. F., Normamatov, A. S., ... & Balakrishnan, C. (2026). A layered Ni (II)-Na (I) coordination polymer: crystal engineering, supramolecular interactions, and functional properties. *Chemical Papers*, 1-18.https://doi.org/10.1007/s11696-026-05251-0
3. Saidov, D. K. U., Turaev, K. K., Kumar, A., Salimova, Z. K., Kholturaev, K. B. U., Ruziev, U. U. U., Normamatov, A. S., Ibragimov, A. B., Adizov, B. Z., Atakhanov, A. A. U., Gao, J., Ibragimov, A. B., & Balakrishnan, C. (2026). Structural elucidation, supramolecular interactions, and antifungal activity of a one-dimensional Cu(II) coordination polymer based on 1,10-phenanthroline and isonicotinate. Journal of Solid State Chemistry, 360, 126074.https://doi.org/10.1016/j.jssc.2026.126074
4. Tursunov, B. C. U., Turaev, K. K., Yakubov, Y. Y., Ernazarov, A. A. U., Reddy, V. K., Kholturaev, K. B. U., Ruzmetov, A. K., Normamatov, A. S., Ibragimov, A. B., Musurmonov, M., & Rasulov, A. A. (2026). Solvothermal synthesis and multifunctional characterization of a two-dimensional Mn(II) coordination polymer with dibromoterephthalate linkers: Dielectric, BET, and Hirshfeld surface studies. Next Materials, 13, 103562.https://doi.org/10.1016/j.nxmate.2026.103562
5. Ugli Kholturaev K. B., Turaev K. K., Salimova Z. K., Adinaev K. F., ugli Ruziev U. U., ugli Saidov D. K., ... & Ibragimov A. B. Integrating structural and textural evidence for a Cd(II) coordination polymer assembled from isonicotinate. *Polyhedron*, 2026, 118299.https://doi.org/10.1016/j.poly.2026.118299