SYNTHESIS AND PXRD ANALYSIS OF A NEW COPPER-EDTA METAL-ORGANIC FRAMEWORK

[a]Abdullaev Ahrorjon Khabibjonovich
[a]PhD, first-year doctoral student at Fergana State University

[b]Mamatqulova Surayyo Abdusamatovna
[b]DSc, Professor Head of the Department of Chemistry, Fergana state university

[d]Aziz Bakhtiyarovich Ibragimov
[d]DSc, Professor, Director of Institute of General and Inorganic Chemistry of Uzbekistan Academy of Sciences.

Abstract
A novel copper-based metal-organic framework (MOF), catena-[dichloro-(μ_4-ethylenediaminetetraacetato)-dicopper], was synthesized via hydrothermal methods using copper(II) chloride and EDTA disodium salt. Structural characterization confirmed a tetragonal crystal system (space group $I4_1/a$) with a distorted square-pyramidal coordination geometry around Cu(II) centers, forming a robust 3D framework hosting void spaces (2528.8 Å^3).
Keywords: Metal-organic framework (MOF); Copper-EDTA complex.

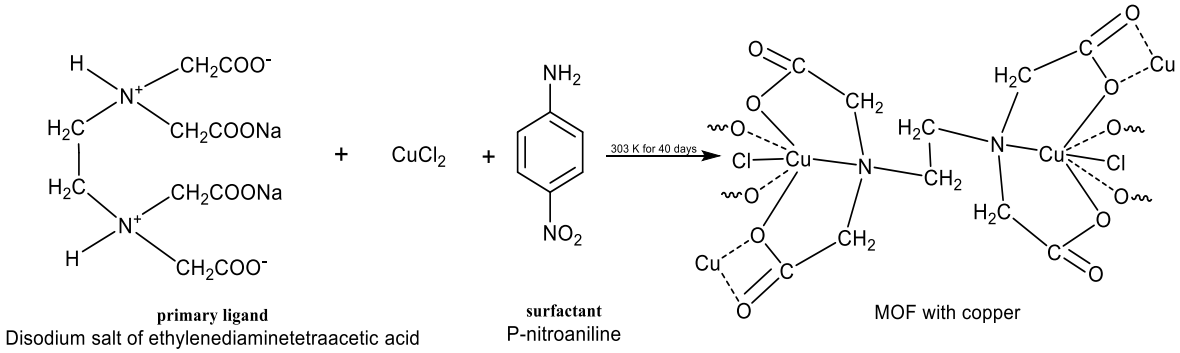
INTRODUCTION

Metal-organic frameworks (MOFs) represent a revolutionary class of porous crystalline materials formed by the self-assembly of metal ions or clusters with multidentate organic linkers. Their unparalleled structural diversity, ultrahigh surface areas (exceeding 7,000 m²/g), and tunable pore functionalities have positioned MOFs at the forefront of materials science for applications spanning gas storage, separation, catalysis, sensing, and energy conversion [1–5]. Among these, the development of MOFs with high proton conductivity has emerged as a critical research frontier, driven by the urgent need for advanced proton-exchange membranes (PEMs) in fuel cells—a cornerstone technology for sustainable energy systems [6–8]. Conventional PEMs like Nafion® suffer from inherent limitations, including dehydration-induced conductivity loss above 80°C, fuel crossover, and restricted operational control under low humidity [9,10]. MOFs offer a compelling alternative: their crystallinity enables precise engineering of proton-conducting pathways, while their porosity permits strategic incorporation of proton carriers (e.g., water, imidazole, or acidic groups).

Synthesis. The synthesis process commenced with the utilization of a hydrothermal method for the sample. Initially, the first solution was meticulously prepared by dissolving 0.06 mmol of the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA-H_2Na_2 · 2H2O) ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) in 0.3 mol of distilled water. Simultaneously, the second solution was created by dissolving 0.117 mmol of Copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$) in 0.3 mol of distilled water.

Additionally, 0.145 mmol of p-nitroaniline ($C_6H_6N_2O_2$) was dissolved in 0.1 mol of ethyl alcohol (C_2H_6O).

Following the preparation of the solutions, the first and second solutions were methodically combined, and the resultant mixture was gradually introduced to the third solution. After a designated period, a white precipitate manifested. Dimethylformamide was subsequently added until the precipitate dissolved, resulting in the formation of a blue cloudy solution. This solution was then placed in a thermostat at a controlled temperature of 303K for an extended duration of 40 days to facilitate crystal growth. Yield: 60% (based on Cu): Anal. calcd. for **1**: $C_5H_6ClCuNO_4$: C, 14.6%; H, 2.5%; O, 26.3%; N, 5.7%; Found: C, 14.3 %; H, 2.2%; O, 26.1%; N, 5.4 %.



Scheme 1. Synthesis of **1.**

PXRD analysis

The crystal structure properties of the metal-organic framework compound catena[dichloro- (μ4-ethylenediaminetetraacetato) -dicopper] were thoroughly investigated using powder X-ray diffraction (PXRD). The diffractogram obtained through PXRD analysis exhibited sharp and distinct peaks, indicating high phase purity and well-ordered crystal structure in the sample.

According to the PXRD results, several characteristic intense peaks were recorded in the diffractogram. The most intense peaks were observed at the following 2θ values: 6.8°, 8.1°, 9.2°, 11.3°, 15.2°, 17.4°, 20.5°, 22.6°, 25.1°, 27.3°, 30.4°, 32.5°, 34.9°, 38.2°, 40.1°, 42.7°, 45.3°, 47.6°, 50.2°, 52.5°, 55.0°, 57.3°, and 59.8°. Notably, the peak with the highest intensity at 6.8° was identified as a characteristic peak confirming the main structural features of the MOF (Fig 1.).

The sharp and intense peaks observed in the PXRD diffractogram indicate the high degree of order in the crystal structure. These results align well with the molecular structure and crystal lattice model determined by X-ray crystallography. X-ray structural analysis confirmed that copper (II) ions form effective coordination with ligand molecules, resulting in a three-dimensional stable and ordered coordination polymer.

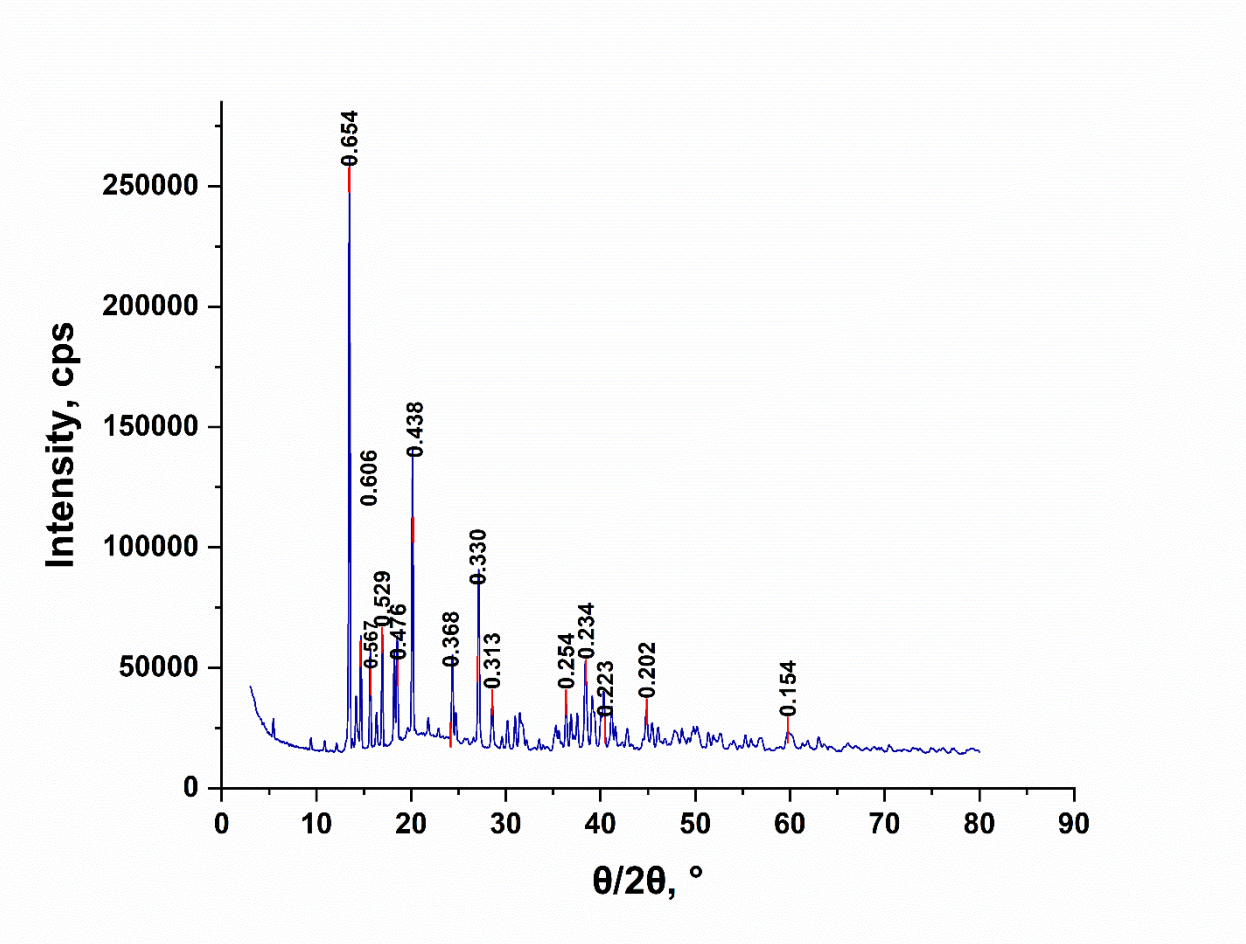


Figure 1. PXRD patters of 1.

CONCLUSION

This study successfully synthesized and characterized catena-[dichloro-(μ4-ethylenediaminetetraacetato)-dicopper], a Cu(II)-EDTA MOF with a unique 3D tetragonal framework.

REFERENCES

1. H. Furukawa, K.E. Cordova, M. O’Keeffe, O.M. Yaghi, The Chemistry and Applications of Metal-Organic Frameworks, Science 341 (2013) 1230444. https://doi.org/10.1126/science.1230444.

2. H.-C. Zhou, J.R. Long, O.M. Yaghi, Introduction to Metal–Organic Frameworks, Chem. Rev. 112 (2012) 673–674. https://doi.org/10.1021/cr300014x.

3. N. Stock, S. Biswas, Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites, Chem. Rev. 112 (2012) 933–969. https://doi.org/10.1021/cr200304e.

4. H. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, Nature 402 (1999) 276–279. https://doi.org/10.1038/46248.

5. M.J. Kalmutzki, C.S. Diercks, O.M. Yaghi, Metal–Organic Frameworks for Water Harvesting from Air, Advanced Materials 30 (2018) 1704304. https://doi.org/10.1002/adma.201704304.

6. D.R. Dekel, Review of cell performance in anion exchange membrane fuel cells, Journal of Power Sources 375 (2018) 158–169. https://doi.org/10.1016/j.jpowsour.2017.07.117.

7. P. Ramaswamy, N.E. Wong, G.K.H. Shimizu, MOFs as proton conductors – challenges and opportunities, Chem. Soc. Rev. 43 (2014) 5913–5932. https://doi.org/10.1039/C4CS00093E.

8. D.-W. Lim, H. Kitagawa, Proton Transport in Metal–Organic Frameworks, Chem. Rev. 120 (2020) 8416–8467. https://doi.org/10.1021/acs.chemrev.9b00842.

9. K.A. Mauritz, R.B. Moore, State of Understanding of Nafion, Chem. Rev. 104 (2004) 4535–4586. https://doi.org/10.1021/cr0207123.

10. M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative Polymer Systems for Proton Exchange Membranes (PEMs), Chem. Rev. 104 (2004) 4587–4612. https://doi.org/10.1021/cr020711a.