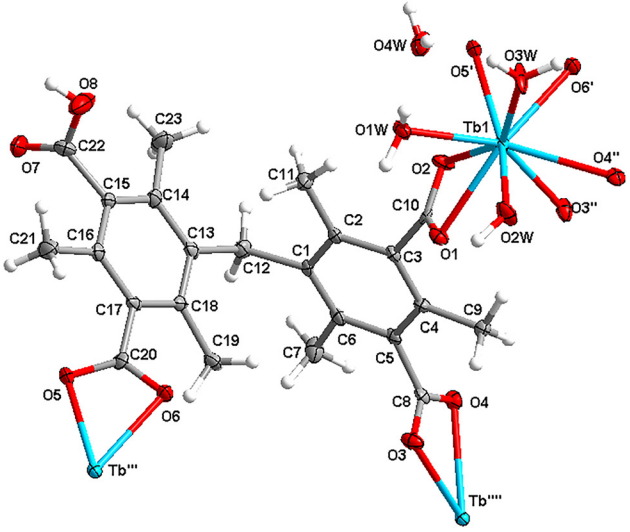
Yanwen Sun, Yanzi Li, Xinyu Zhang, Jiayi Wu, Yongzhen Zhang and Zhen Chen*

Crystal structure of poly[diaqua-μ_3-(5-(3,5-dicarboxy-2,4,6-trimethylbenzyl)-2,4,6-trimethylisophthalato)-κ^6O,O′:O″,O‴:O⁗,O⁗′) terbium(III)-monohydrate], $C_{23}H_{28}TbO_{12}$



https://doi.org/10.1515/ncrs-2025-0235
Received May 20, 2025; accepted July 2, 2025;
published online August 1, 2025

Abstract

$C_{23}H_{28}TbO_{12}$, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.5571(5) Å, b = 11.4427(7) Å, c = 24.8022(15) Å, V = 2428.5(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0254, $wR_{ref}(F^2)$ = 0.0466, T = 293(2) K.

CCDC no.: 2449500

***Corresponding author: Zhen Chen**, School of Chemistry and Chemical Engineering, Hebei Minzu Normal University, Higher Education Park, Chengde, 067000, P.R. China, E-mail: chenzhenas@126.com. https://orcid.org/0000-0001-5299-7365

Yanwen Sun, Xinyu Zhang, Jiayi Wu and Yongzhen Zhang, School of Chemistry and Chemical Engineering, Hebei Minzu Normal University, Higher Education Park, Chengde, 067000, P.R. China

Yanzi Li, School of Chemistry and Chemical Engineering, Hebei Minzu Normal University, Higher Education Park, Chengde, 067000, P.R. China; and Asset and Laboratory Management Center, Hebei Minzu Normal University, Higher Education Park, Chengde, 067000, P.R. China

Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	0.35 × 0.10 × 0.10 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	2.98 mm^{-1}
Diffractometer, scan mode:	Bruker APEX2, φ and ω scans
θ_{max}, completeness:	27.5°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14354, 5506, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5150
$N(param)_{refined}$:	337
Programs:	Bruker,[1] Olex2,[2] SHELX,[3,4] Diamond[5]

The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

An aqueous solution (0.5 ml) containing $Tb(NO_3)_3{\cdot}6H_2O$ (6.0 mg) and $H_3PW_{12}O_{40}{\cdot}xH_2O$ (4.0 mg) was added into a glass tube. Then, the aqueous solution of tetrabutylammonium bromide (4 mg/ml) 0.25 ml was added. Next, a solution of 5,5′-methylenebis (2,4,6-trimethylisophthalic acid) (H_4BTMIPA) (4.0 mg) in cyclohexanol and toluene (1:1 v/v, 0.5 ml) was layered on the aqueous solution. The glass tube was heated slowly to 363 K from room temperature in 300 min, kept at 363 K for 3 min and then cooled slowly to 303 K over a period of 600 min. Colourless rod-shaped crystals formed suitable for single crystal X-ray structure.

2 Experimental details

The structure was solved by Direct Methods with the SHELX.[3] All H-atoms were positioned geometrically and refined using a riding model with d(C–H) = 0.93 Å, U_{iso} = 1.2U_{eq}(C) for

aromatic, 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2, 0.96 Å, U_{iso} = 1.5U_{eq} (C) for CH_3 atoms and d(O–H) = 0.85 Å, U_{iso} = 1.2U_{eq} (O) for H_2O.

3 Comment

In recent years, metal-organic frameworks have attracted extensive attention due to their controllable structures and a wide variety of potential applications.[6–9] As one special type of MOF materials, the lanthanide MOFs have outstanding performances in fluorescent and photochromic materials[10,11] and many excellent Ln–MOFs were used for sensing metal ions or organic molecules.[12] Our team has also developed an europium-organic framework which can sense Fe^{3+} and Al^{3+} through fluorescence quenching and enhancement, respectively.[13] The Ln–MOFs may have different properties depending on their ion centers. The Tb^{3+} and Tb–MOFs usually exhibit strong fluorescence emission in the visible light region.[14,15] This property may endow it with unique application value in fields such as luminescent materials and fluorescence sensing. In this work, we report the crystal structure of a terbium-based framework.

The asymmetric unit cell was found to contain one Tb^{3+} ion, an incompletely deprotonated HBTMIPA ligand, one hydroxyl group, two coordination water molecules and one lattice water molecule. The central Tb^{3+} is located within a subtly distorted nine-coordination sphere. This sphere is defined by six oxygen atoms stemming from three distinct HBTMIPA ligands, one coordinated hydroxyl group and two coordinated water molecules. The lengths of the Tb–O bonds span a narrow range from 2.303(3) to 2.640(3) Å. Each BTMIPA ligand connects three Tb^{3+} ions by means of its three carboxylate groups. Significantly, all these carboxylate groups assume a chelating coordination mode, which is different with the coordination mode in previously reported Ln-framwork.[13] Consequently, the central Tb^{3+} ions were interconnected via BTMIPA ligands, thereby generating a one - dimensional wavy structure oriented in the [010] direction. Adjacent wavy structures are linked to form a two – dimensional structure through O–H···O hydrogen bonds (O1W···$O4_{\$1}$ = 2.8149(2) Å and O1W–H1WB···$O4_{\$1}$ = 161.252(5)°, symmetry code: \$1 = 1 + X, Y, Z) in [100] direction. The extended three-dimensional supramolecular structure was formed by other O–H···O hydrogen bonds (O8···$O2_{\$2}$ = 2.6657(1) Å and O8–H8···$O2_{\$2}$ = 127.330(4)°, symmetry code: \$2 = –1/2 + X, –1/2–Y, –1–Z).

Acknowledgments: We are grateful to the team of the High-Quality Experimental Courses of Hebei Minzu Normal University for their support in terms of venues and guidance provided for certain experiments.

Research funding: This research is funded by S&T program of Chengde (No. HZLC2024020), Hebei Provincial College Students' Innovation and Entrepreneurship Training Program Project, Hebei Minzu Normal University Postgraduate Funding Project (No. HQ2025003) and the Construction Project of High-Quality Experimental Courses of Hebei Minzu Normal University.

References

1. Bruker. *Sadabs*, *Saint and Smart*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. Olex2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
3. Sheldrick, G. M. A Short History of Shelx. *Acta Crystallogr.* **2008**, *A64*, 112–122.
4. Sheldrick, G. M. Crystal Structure Refinement with Shelxl. *Acta Crystallogr.* **2015**, *C71*, 3–8.
5. Brandenburg, K. *Diamond. Visual Crystal Structure Information System. Ver. 4.0*; Crystal Impact: Bonn, Germany, 2015.
6. Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 673–674.
7. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.
8. Yusuf, F. V.; Malek, N. I.; Kailasa, S. K. Review on Metal-Organic Framework Classification, Synthetic Approaches, and Influencing Factors: Applications in Energy, Drug Delivery, and Wastewater Treatment. *ACS Omega* **2022**, *7*, 44507–44531.
9. Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun, Y. J.; Qin, J. S.; Yang, X. Y.; Zhang, P.; Wang, Q.; Zou, L. F.; Zhang, Y. M.; Zhang, L. L.; Fang, Y.; Li, J. L.; Zhou, H. C. Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. *Adv. Mater.* **2018**, *30*, 1704303–1704337.
10. Li, Q. P.; Du, S. W. A Family of 3D Lanthanide Organic Frameworks with Tunable Luminescence and Slow Magnetic Relaxation. *RSC Adv.* **2015**, *5*, 9898–9903.
11. Liu, Q. Y.; Wang, W. F.; Wang, Y. L.; Shan, Z. M.; Wang, M. S.; Tang, J. K. Diversity of Lanthanide(III)-Organic Extended Frameworks with a 4,8-Disulfonyl-2,6-Naphthalenedicarboxylic Acid Ligand: Syntheses, Structures, and Magnetic and Luminescent Properties. *Inorg. Chem.* **2012**, *51*, 2381–2392.
12. Lustig, W.; Mukherjee, S.; Rudd, N.; Desai, A.; Li, J.; Ghosh, S. Metal-Organic Frameworks: Functional Luminescent and Photonic Materials for Sensing Applications. *Chem. Soc. Rev.* **2017**, *46*, 3242.
13. Chen, Z.; Sun, Y. W.; Zhang, L. L.; Sun, D.; Liu, F. L.; Meng, Q. G.; Wang, R. M.; Sun, D. F. A Tubular Europium-Organic Framework Exhibiting Selective Sensing of Fe^{3+} and Al^{3+} Over Mixed Metal Ions. *Chem. Commun.* **2013**, *49*, 11557–11559.
14. Wang, X. F.; Chu, C. X.; Wu, Y. W.; Deng, Y. Y.; Zhou, J.; Yang, M.; Zhang, S. Y.; Huo, D. Q.; Hou, C. J. Synthesis of Yttrium(III)-Based Rare-Earth Metal-Organic Framework Nanoplates and its Applications for Sensing of Fluoride Ions and Ph. *Sensors Actuators B: Chem.* **2020**, *321*, 128455.
15. Sun, Y.; Chen, Z.; Wang, X.; Wang, L.; Yang, X.; Liang, X.; Fan, S.; Zhang, P. Novel Ba^{2+} and Pb^{2+} Metal-Organic Frameworks Based on a Semi-Rigid Tetra-Carb-Oxy-Lic Acid: Syntheses, Structures, Topologies and Luminescence Properties. *Acta Crystallogr., Sect. C: Struct. Chem.* **2021**, *77*, 291.