Guoqiang Li, Guo Chen, Yanping Liu, Gao Wang and Liyu Liu*

The crystal structure of poly[bis(*N,N*-dimethylformamide- $\kappa^1 O$)(μ_4 -2',5,5',5''-tetracarboxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylato- $\kappa^4 O:O':O'':O'''$) manganese(II)] – *N,N*-dimethylformamide (1/2), $C_{36}H_{40}N_4O_{16}Mn$

<https://doi.org/10.1515/ncrs-2020-0118>

Received March 3, 2020; accepted May 11, 2020; available online May 29, 2020

***Corresponding author: Liyu Liu**, Chongqing Key Laboratory of Soft Condensed Matter Physics and Smart, Materials, College of Physics, Chongqing University, Chongqing 401331, P.R. China, e-mail: lyliu@cqu.edu.cn

Guoqiang Li, Guo Chen, Yanping Liu and Gao Wang: Chongqing Key Laboratory of Soft Condensed Matter Physics and Smart, Materials, College of Physics, Chongqing University, Chongqing 401331, P.R. China. <https://orcid.org/0000-0002-1073-4214> (G. Li)

Abstract

$C_{36}H_{40}N_4O_{16}Mn$, monoclinic, $P2_1/c$ (no. 14), $a = 10.5247(11)$ Å, $b = 19.0823(19)$ Å, $c = 10.5502(11)$ Å, $\beta = 112.641(2)^\circ$, $V = 1955.6(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0619$, $wR_{ref}(F^2) = 0.1741$, $T = 296$ K.

CCDC no.: 1497238

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.22 \times 0.20 \times 0.18$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.42 mm^{-1}
Diffractometer, scan mode:	Bruker APEXII, φ and ω
$\theta_{\max}$, completeness:	25.7° , 80%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8312, 3009, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1925
$N(\text{param})_{\text{refined}}$:	297
Programs:	Bruker Programs [1], SHELX [2]

Source of material

The educt [1,1':4',1''-terphenyl]-2',3,3'',5,5',5''-hexacarboxylic acid (H_6L) was purchased from Jinan Camolai Trading Company (China), and other reagents were A. R. grade also commercially available and used as received. A mixture of H_6L (98.9 mg, 0.2 mmol), $Mn(OAc)_2 \cdot 4 H_2O$ (49.1 mg, 0.2 mmol), and 10 mL DMF were placed in a 15 mL Teflon-lined autoclave at 413 K for 3 days, then cooled to room temperature. Colorless block crystals were obtained in a yield of 48% (based on Mn).

Experimental details

The structure was solved by direct methods and refined using the SHELX software [2]. All of the hydrogen atoms were placed in the calculated positions. Both DMF molecules show a disorder (see Table 2).

Comment

Recently, the multi-carboxylate biphenyl-type ligand has received much more attention than ever before because of its

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Mn1	0.0000	0.0000	0.5000	0.0235(3)
O1	0.1708(3)	0.00035(14)	0.7008(3)	0.0385(7)
O2	0.3050(3)	0.08709(14)	0.6807(3)	0.0345(7)
H2	0.2347	0.1098	0.6406	0.052 [*]
O3	0.4596(3)	0.38890(15)	1.0035(3)	0.0433(8)
O4	0.6414(3)	0.31953(15)	1.0615(4)	0.0480(9)
O5	−0.0011(4)	0.29172(18)	0.8388(5)	0.0587(10)
H5 ^a	−0.0845	0.2918	0.8187	0.088 [*]
O6	−0.0348(4)	0.17732(19)	0.8296(5)	0.0595(10)
H6 ^b	−0.1119	0.1891	0.8234	0.089 [*]
O7	−0.1415(4)	−0.01374(18)	0.6020(4)	0.0538(10)
O8A ^a	−0.2557(13)	0.3184(7)	0.7561(16)	0.110(5)
O8 ^b	−0.2931(13)	0.2019(8)	0.7468(16)	0.127(5)
N1	−0.2777(8)	0.0147(3)	0.7123(8)	0.094(2)
N2	−0.4734(8)	0.2904(4)	0.6790(6)	0.0914(18)
C1	0.2781(4)	0.0366(2)	0.7422(4)	0.0260(8)
C2	0.3890(4)	0.01779(19)	0.8792(4)	0.0238(8)
C3	0.4419(4)	−0.05021(19)	0.9005(4)	0.0256(9)
H3	0.4020	−0.0839	0.8330	0.031 [*]
C4	0.4484(4)	0.06903(19)	0.9812(4)	0.0225(8)
C5	0.3895(4)	0.14157(19)	0.9662(4)	0.0240(8)
C6	0.4772(4)	0.2000(2)	1.0006(4)	0.0253(9)
H6A	0.5722	0.1939	1.0341	0.030 [*]
C7	0.4212(4)	0.26740(19)	0.9844(4)	0.0261(9)
C8	0.5121(4)	0.3305(2)	1.0185(4)	0.0292(9)
C9	0.2800(4)	0.27675(19)	0.9374(4)	0.0283(9)
H9	0.2433	0.3217	0.9268	0.034 [*]
C10	0.1944(4)	0.2198(2)	0.9067(4)	0.0295(9)
C11	0.0416(5)	0.2301(3)	0.8539(5)	0.0392(11)
C12	0.2495(4)	0.1526(2)	0.9220(4)	0.0284(9)
H12	0.1905	0.1142	0.9021	0.034 [*]
C13	−0.1745(8)	0.0222(4)	0.6726(8)	0.082(2)
H13	−0.1204	0.0619	0.7057	0.098 [*]
C14 ^c	−0.396(2)	−0.0246(17)	0.626(3)	0.134(7)
H14A ^c	−0.4508	0.0038	0.5496	0.202 [*]
H14B ^c	−0.4493	−0.0380	0.6781	0.202 [*]
H14C ^c	−0.3660	−0.0658	0.5932	0.202 [*]
C14A ^d	−0.3655(17)	−0.0480(8)	0.6769(17)	0.084(4)
H14D ^d	−0.4605	−0.0342	0.6433	0.126 [*]
H14E ^d	−0.3448	−0.0767	0.7571	0.126 [*]
H14F ^d	−0.3486	−0.0741	0.6072	0.126 [*]
C15A ^d	−0.3213(18)	0.0658(8)	0.7897(17)	0.088(4)
H15A ^d	−0.4014	0.0901	0.7288	0.132 [*]
H15B ^d	−0.2484	0.0989	0.8321	0.132 [*]
H15C ^d	−0.3429	0.0423	0.8593	0.132 [*]
C15 ^c	−0.248(3)	0.0398(15)	0.875(3)	0.133(7)
H15D ^c	−0.2675	0.0889	0.8758	0.200 [*]
H15E ^c	−0.1540	0.0310	0.9323	0.200 [*]
H15F ^c	−0.3073	0.0138	0.9079	0.200 [*]
C16	−0.3254(12)	0.2785(7)	0.7343(10)	0.118(3)
H16	−0.2931	0.2327	0.7503	0.141 [*]
H16A	−0.2597	0.3139	0.7586	0.141 [*]
C17	−0.5581(11)	0.2328(5)	0.6410(10)	0.118(3)
H17A	−0.5120	0.1955	0.6148	0.178 [*]
H17B	−0.6411	0.2448	0.5647	0.178 [*]

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H17C	−0.5805	0.2179	0.7168	0.178 [*]
C18	−0.5168(16)	0.3568(7)	0.6616(15)	0.187(5)
H18A	−0.4703	0.3825	0.7448	0.281 [*]
H18B	−0.6142	0.3580	0.6390	0.281 [*]
H18C	−0.4968	0.3775	0.5883	0.281 [*]

^aOccupancy: 0.496(12), ^bOccupancy: 0.504(12), ^cOccupancy: 0.44(2), ^dOccupancy: 0.56(2).

carboxylate groups may be completely or partially deprotonated to induce versatile coordination modes and the rotation of the formal C—C single bond between phenyl rings to generate different conformations [3, 4]. As a typical multicarboxylate biphenyl-type ligand, *H₆L* has been employed to construct the porous metal-organic frameworks *MOFs* by coordinating with ds-, d- and f- block elements, such as Cu(II) [5], Zn(II) [6], Eu(III) [7] and so on. However, to the best of our knowledge, the crystal structure which contains *H₆L* and a related deprotonated anion, respectively with manganese(II) have not been reported so far. This contribution is part of our continuing interest in the synthesis and characterisation of *MOFs* with —COOH groups.

The asymmetric unit of the title structure is shown in the upper view of the figure, comprising one half of a Mn(II), one half of the dianionic *H₄L*^{2−} ligand, one coordinated *N,N*-dimethylformamide and one additional *N,N*-dimethylformamide molecule. The central Mn(II) shows a hexa-coordinated environment in form of a distorted octahedral [MnO₆] geometry, in which the equatorial plane is occupied by four carboxyl/carboxylate oxygen atoms (O1, O1#, O3 and O3#) derived from four *H₂L*^{4−} ligands and two amide oxygen atoms (O7 and O7#) derived from *N,N*-dimethylformamide found in axial positions. Among them, all the bond angles around the Mn(II) atom vary from 85.76(12)° to 180° and the Mn—O bond lengths are in the range of 2.163(3) Å–2.188(3) Å, which are comparable to those reported for the related [MnO₆] geometry [8, 9]. A noteworthy feature of the structure is that the bond angles of O1–Mn1–O1#, O3–Mn1–O3#, O7–Mn1–O7# are equal to 180° and the maximum difference of Mn—O bond length is only 0.025 Å, which further indicates that the distortion of the octahedral [MnO₆] geometry is small.

Moreover, as shown in the lower view of the figure (all solvent molecules and hydrogen atoms have been omitted), two perpendicular one-dimensional chains are formed along the *a*-axis and *b*-axis by the metal ions connected with terminal and intermediate carboxyl groups of the ligand, respectively. Then, the chains are connected with each other by sharing the [MnO₆] clusters to generate a highly ordered 2D

metal-organic framework with a porous structure and containing noncoordinated DMF molecules in the pores (lower part of the figure). The title structure enriches the structural chemistry of terphenyl-carboxylato ligands [10].

Acknowledgements: We gratefully acknowledge support by the Fundamental and Advanced Research Program of Chongqing cstc2018jcyjAX0009 and cstc2019jcyj-msxmX0477, the National Natural Science Foundation of China (11974066 and 11674043) and the Fundamental Research Funds for the Central Universities 2019CDYGYB007.

References

1. Bruker: APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Zhang, W. H.; Dong, Z.; Wang, Y. Y.; Hou, L.; Jin, J. C.; Huang, W. H.; Shi, Q. Z.: Synthesis, structural diversity and fluorescent characterisation of a series of d^{10} metal-organic frameworks (MOFs): reaction conditions, secondary ligand and metal effects. *Dalton Trans.* **40** (2011) 2509–2521.
4. Wang, J. J.; Lv, J. F.; Cao, P. X.; Zhang, M. L.; Gao, L. J.; Lv, L.; Ren, Y. X.; Hou, X. Y.: Effect of metal ions on the structures of coordination polymers based on biphenyl-2,2', 4,4'-tetracarboxylate. *Z. Anorg. Allg. Chem.* **637** (2011) 1585–1589.
5. Zhang, Q.; Yu, J. C.; Cai, J. F.; Song, R. J.; Cui, Y. J.; Yang, Y.; Chen, B. L.; Qian, G. D.: A porous metal-organic framework with –COOH groups for highly efficient pollutant removal. **50** (2014) 14455–14458.
6. Gai, Y. L.; Jiang, F. L.; Chen, L.; Wu, M. Y.; Su, K. Z.; Pan, J.; Wan, X. Y.; Hong, M. C.: Europium and terbium coordination polymers assembled from hexacarboxylate ligands: structures and luminescent properties. *Cryst. Growth Des.* **14** (2014) 1010–1017.
7. Wan, X. Y.; Jiang, F. L.; Chen, L.; Wu, M. Y.; Zhang, M. J.; Pan, J.; Su, K. Z.; Yang, Y.; Hong, M. C.: Structural diversity modulated by the ratios of a ternary solvent mixture: syntheses, structures, and luminescent properties of five Zinc(II) metal-organic frameworks. *Cryst. Growth Des.* **15** (2015) 1481–1491.
8. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of bis(ammonium) diaqua-tetrakis(4-hydroxybenzoato)-manganese(II) tetrahydrate, $[NH_4]_2[C_{28}H_{24}MnO_{14}] \cdot 4(H_2O)$. *Z. Kristallogr. NCS* **235** (2020) 313–315.
9. Zhu, L.; Zhou, T.: Crystal structure of diaqua-bis[1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluor-4-oxo-1,4-dihydroquinolin-3-carboxylic acid] manganese(II)-benzene-1-carboxyl-4-carboxylate octahydrate, $C_{54}H_{74}F_2MnN_6O_{24}$. *Z. Kristallogr. NCS* **230** (2015) 265–266.
10. Li, W.; Mai, S. L. J.: Crystal structure of poly[diaqua-(μ_8 -1,1':2',1''-terphenyl-3,3'',4',5'-tetracarboxylato- $\kappa^8 O^1:O^2:O^3:O^4:O^5:O^6:O^7:O^8$)dicopper(II)], $C_{22}H_{14}Cu_2O_{10}$. *Z. Kristallogr. NCS* **234** (2019) 849–850.