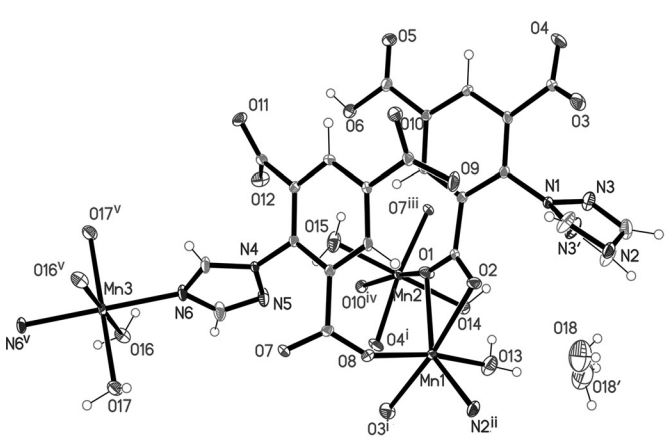
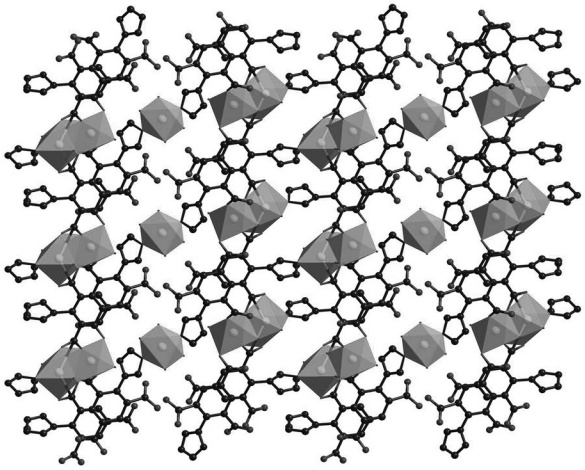
Yan-Yan An*, Juan-Zhi Yan* and Dan Zhan

Crystal structure of poly[deca aqua-bis(μ_4-2-(triazol-1-yl)-benzene-1,3,5-tricarboxylato)-bis(μ_5-2-(triazol-1-yl)-benzene-1,3-dicarboxylato-5-carboxyl acid) pentamanganese(II)] dihydrate, $C_{44}H_{42}Mn_5N_{12}O_{36}$





https://doi.org/10.1515/ncrs-2022-0136
Received March 21, 2022; accepted July 4, 2022;
published online July 21, 2022

Abstract

$C_{44}H_{42}Mn_5N_{12}O_{36}$, triclinic, $P\bar{1}$ (no. 2), a = 7.6398(7) Å, b = 9.9043(5) Å, c = 20.1160(13) Å, α = 87.300(5)°, β = 81.868(6)°, γ = 67.555(7)°, V = 1392.62(18) Å^3, Z = 1, $R_{gt}(F)$ = 0.0554, w$R_{ref}(F^2)$ = 0.1446, T = 293(2) K.

CCDC no.: 2034133

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:	0.12 × 0.12 × 0.11 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	10.1 mm^{-1}
Diffractometer, scan mode:	Xcalibur,
θ_{max}, completeness:	71.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9402, 5274, 0.052
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4024
$N(param)_{refined}$:	469
Programs:	CrysAlis^{PRO} [1, 2], SHELX [3, 4]

Source of material

All chemicals were available from commercial sources. $MnCl_2{\cdot}6H_2O$ (0.171 mmol), 2-(4*H*-1,2,4-triazol-4-yl)benzene-1,3,5-tricarboxylic acid (0.097 mmol) and H_2O/CH_3CN (4 mL, 1:3 v/v) were placed in a 15 mL PTFE vessel sealed with stainless steel reactor, heated to 120 °C for three days. Colorless crystals of the title compound with a yield of 49% were obtained through the cooling process (2 °C h^{-1}). **Elemental analysis** found/calcd. (%) for $C_{44}H_{42}Mn_5N_{12}O_{36}$: C 33.22/33.34, H 2.64/2.56, N 10.57/10.43. IR data

***Corresponding authors: Yan-Yan An and Juan-Zhi Yan,** Department of Materials Science and Chemical Engineering, Taiyuan University, Taiyuan 030032, P. R. China, E-mail: anyanyan@tyu.edu.cn (Y.-Y. An), yanjuanzh@tyu.edu.cn (J.-Z. Yan).
https://orcid.org/0000-0003-0070-5417 (Y.-Y. An)
Dan Zhan, Department of Materials Science and Chemical Engineering, Taiyuan University, Taiyuan 030032, P. R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.45071 (10)	0.28163 (8)	0.39359 (3)	0.01672 (18)
Mn2	0.09647 (10)	0.37918 (8)	0.27257 (3)	0.01573 (18)
Mn3	1.000000	0.500000	0.000000	0.0165 (2)
N1	0.3360 (5)	−0.1919 (4)	0.41308 (18)	0.0167 (8)
N2	0.4059 (6)	−0.2316 (4)	0.51512 (19)	0.0237 (9)
N3[a]	0.1741 (18)	−0.1842 (19)	0.4510 (6)	0.032 (3)
N3′[b]	0.1746 (12)	−0.1000 (13)	0.4530 (4)	0.036 (2)
N4	0.7642 (5)	0.2476 (4)	0.14042 (17)	0.0143 (7)
N5	0.6311 (6)	0.3810 (4)	0.1596 (2)	0.0310 (10)
N6	0.8424 (5)	0.4011 (4)	0.0749 (2)	0.0213 (8)
O1	0.3114 (5)	0.1948 (3)	0.32006 (17)	0.0253 (7)
O2	0.4665 (5)	0.0397 (4)	0.39225 (16)	0.0248 (7)
O3	0.4345 (6)	−0.4936 (4)	0.38126 (18)	0.0327 (9)
O4	0.2547 (6)	−0.5069 (4)	0.30786 (19)	0.0343 (9)
O5	0.2717 (6)	−0.2287 (4)	0.10105 (18)	0.0380 (10)
O6	0.3103 (6)	−0.0180 (4)	0.10497 (16)	0.0306 (8)
H6	0.296782	−0.014717	0.065129	0.046*
O7	0.9507 (5)	0.2483 (3)	0.25107 (16)	0.0218 (7)
O8	0.7386 (5)	0.2312 (4)	0.33643 (16)	0.0252 (7)
O9	0.7816 (5)	−0.3036 (4)	0.31846 (17)	0.0324 (9)
O10	0.9299 (5)	−0.4168 (3)	0.22121 (16)	0.0227 (7)
O11	0.7504 (5)	−0.0354 (4)	0.01712 (16)	0.0267 (8)
O12	0.5428 (5)	0.1776 (4)	0.06150 (17)	0.0300 (8)
O13	0.1755 (5)	0.3567 (4)	0.45747 (19)	0.0405 (10)
H13B	0.094071	0.340659	0.437700	0.061*
H13C	0.187311	0.310359	0.494270	0.061*
O14	−0.1019 (5)	0.4346 (4)	0.36933 (17)	0.0252 (8)
H14A	−0.202822	0.507581	0.363504	0.038*
H14B	−0.130931	0.361752	0.381934	0.038*
O15	0.2838 (5)	0.3252 (4)	0.17842 (19)	0.0398 (10)
H15C	0.380998	0.347059	0.178917	0.048*
H15B	0.315387	0.234429	0.171627	0.048*
O16	0.7442 (5)	0.6988 (3)	0.01266 (18)	0.0269 (8)
H16A	0.762504	0.764711	−0.012586	0.040*
H16B	0.650745	0.681982	0.001894	0.040*
O17	1.0954 (5)	0.5777 (4)	0.08392 (17)	0.0311 (8)
H17A	1.165719	0.623903	0.068315	0.047*
H17C	1.158958	0.504873	0.106295	0.047*
O18[c]	0.1901 (17)	0.1530 (15)	0.5542 (6)	0.079 (3)
H18C[c]	0.084980	0.140562	0.558641	0.095*
H18D[c]	0.270661	0.083422	0.573491	0.095*
O18′[d]	0.099 (3)	0.242 (3)	0.5697 (8)	0.082 (5)
H18G[d]	0.139287	0.266968	0.602443	0.098*
H18E[d]	−0.021893	0.266337	0.577582	0.098*
C1	0.3725 (6)	0.0667 (5)	0.3443 (2)	0.0162 (9)
C2	0.3403 (6)	−0.0531 (5)	0.3100 (2)	0.0146 (8)
C3	0.3392 (6)	−0.1815 (5)	0.3416 (2)	0.0157 (9)
C4	0.3244 (6)	−0.2938 (5)	0.3061 (2)	0.0164 (9)
C5	0.3092 (6)	−0.2754 (5)	0.2380 (2)	0.0174 (9)
H5	0.299379	−0.349246	0.213713	0.021*
C6	0.3085 (6)	−0.1486 (5)	0.2056 (2)	0.0145 (9)
C7	0.3258 (6)	−0.0385 (5)	0.2416 (2)	0.0156 (9)
H7	0.327674	0.045766	0.219666	0.019*
C8	0.4714 (8)	−0.2500 (6)	0.4519 (3)	0.0363 (13)
H8	0.599808	−0.298748	0.435626	0.044*
C9[a]	0.2164 (16)	−0.210 (2)	0.5140 (7)	0.034 (3)
H9[a]	0.131097	−0.213067	0.551319	0.041*
C9′[b]	0.2247 (14)	−0.1296 (15)	0.5129 (5)	0.040 (3)
H9′[b]	0.143744	−0.084873	0.551349	0.048*
C10	0.3365 (7)	−0.4413 (5)	0.3355 (2)	0.0187 (9)
C11	0.2929 (6)	−0.1360 (5)	0.1316 (2)	0.0201 (10)
C12	0.8294 (6)	0.1997 (5)	0.2785 (2)	0.0169 (9)
C13	0.7973 (6)	0.0888 (5)	0.2378 (2)	0.0145 (9)
C14	0.8128 (6)	−0.0458 (5)	0.2655 (2)	0.0165 (9)
H14	0.827070	−0.062825	0.310684	0.020*
C15	0.8069 (6)	−0.1557 (5)	0.2258 (2)	0.0133 (8)
C16	0.7715 (6)	−0.1266 (5)	0.1596 (2)	0.0166 (9)
H16	0.768023	−0.199819	0.133118	0.020*
C17	0.7415 (6)	0.0111 (5)	0.1326 (2)	0.0152 (9)
C18	0.7663 (6)	0.1133 (5)	0.1712 (2)	0.0144 (8)
C19	0.8421 (6)	−0.3046 (5)	0.2573 (2)	0.0172 (9)
C20	0.6722 (7)	0.0564 (5)	0.0646 (2)	0.0191 (10)
C22	0.8884 (7)	0.2623 (5)	0.0903 (2)	0.0233 (10)
H22	0.992806	0.185713	0.069206	0.028*
C23	0.6854 (8)	0.4694 (6)	0.1189 (3)	0.0332 (12)
H23	0.621033	0.570262	0.120204	0.040*

[a]Occupancy: 0.399 (14). [b]Occupancy: 0.601 (14). [c]Occupancy: 0.606 (16). [d]Occupancy: 0.394 (16).

(KBr, cm^{-1}): 3426 (s), 1037 (s), 1614 (s), 1380 (m), 668 (m), 651 (m), 469 (w), 3727 (w), 2967 (w), 1285 (w), 784 (w), 589 (w), 530 (w), 415 (w).

Experimental details

Hydrogen atoms were generated geometrically. CCDC number 2034133 contains the crystallographic data, which has been deposited in Cambridge Crystallographic Database.

Comment

As a class of porous metal-organic framework materials, MOFs have aroused great attention and focused research due to their structural diversities and the prospects of application in the area of specific gas separation and subsequent storage, heterogeneous catalysis, fluorescence, magnetism, and electrochemistry, etc. [5–7 and references cited there].

With the development of coordination chemistry, the functionally bi-topic ligands including amino polycarboxylic acid [8] and N-containing aromatic carboxylic acid [9] are of considerable interest. Triazole-modified aromatic carboxylic

compounds represent the most important class of heteropolydentate ligands capable of forming mono-, bi-, and polynuclear complexes with inorganic metals [10–13]. We herein report the synthesis and crystal structure of a novel complex $[Mn_5(\mu_4\text{–}L^{3-})_2(\mu_5\text{–}HL^{2-})_2(H_2O)_{10}]\cdot 2H_2O$ (**1**) (H_3L = 2-(4*H*-1,2,4-triazol-4-yl)benzene-1,3,5-tricarboxylic acid). The formula of **1** is established by elemental analysis. Single crystal X-ray diffraction analysis reveals that compound **1** crystallized in the triclinic space group $P\bar{1}$, possessing a 3D structure. The asymmetric unit consists of two and a half crystallographically independent Mn(II) ions, one fully-deprotonated L^{3-} and one partly deprotonated HL^{2-} ligand, five aqua ligands as well as one lattice water molecule (cf. left part of the figure). The six-coordinated Mn1 ion is finished by four O atoms (O1, O2, O3i, O8; i = *x*, *y*+1, *z*) and one N atom from four L^{3-}anions and one water molecule to form a distorted octahedral geometry, with the Mn–O length range of 2.180–2.352 Å. The Mn2 ion is surrounded by four oxygen atoms (O1, O4i, O7iii, O10iv; i = *x*, *y*+1, *z*, iii = *x*–1, *y*, *z*, iv = *x*–1, *y*+1, *z*,) on the equatorial plane, and two water molecules (O14, O15) in the axial positions. Mn3 ion is coordinated by water molecules: O16, O17, O16v, O17v (v = –*x*+2, –*y*+1, –*z*) and two N atoms from HL^{2-} and L^{3-} anions. Mn1 and Mn2 ions are joined by two carboxylate groups to form a $[Mn_2O_2]$ unit with the Mn···Mn separation of 3.719 Å. And each $[Mn_2O_2]$ unit is surrounded by four aromatic tricarboxylic acid molecules, which results in a three-dimensional framework (cf. right part of the figure).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: We gratefully acknowledge support by the Natural Science Foundation of Shanxi Province (202103021223002) and National Natural Science Foundation of China (21671124).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Agilent Technologies. CrysAlis^{PRO}; Agilent Technologies: Santa Clara, CA, USA, 2013.
2. Fejfarová K., Aem B., Dehno A. *Absorption Correction: Analytical*; CrysAlis PRO: Oxford Refinement, 2010.
3. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Liu X. P., Fan W. D., Zhang M. H., Li G. X., Liu H. J., Sun D. F., Zhao L. M., Zhu H. Y., Guo W. Y. Enhancing light hydrocarbon storage and separation through introducing lewis basic nitrogen sites within a carboxylate-decorated copper-organic framework. *Mater. Chem. Front.* 2018, *2*, 1146–1154.
6. Li X. Y., Shi W. J., Wang X. Q., Ma L. N., Hou L., Wang Y. Y. Luminescence modulation, white light emission, and energy transfer in a family of lanthanide metal-organic frameworks based on a planar π-conjugated ligand. *Cryst. Growth Des.* 2017, *17*, 4217–4224.
7. Oar–Arteta L., Wezendonk T., Sun X., Kapteijn F., Gascon J. Metal organic frameworks as precursors for the manufacture of advanced catalytic materials. *Mater. Chem. Front.* 2017, *1*, 1709–1745.
8. Truong K. N., Müller P., Dronskowski R., Englert U. Dynamic uptake and release of water in the mixed-metal EDTA complex $M_3[Yb(EDTA)(CO_3)]$ (M = K, Rb, Cs). *Cryst. Growth Des.* 2017, *17*, 80–88.
9. Li Y. F., Wang D., Liao Z., Kang Y., Ding W. H., Zheng X. J., Jin L. P. Luminescence tuning of the Dy–Zn metal-organic framework and its application in the detection of Fe(III) ions. *J. Mater. Chem. C* 2016, *4*, 4211–4217.
10. Liu K., Shi W., Cheng P. The coordination chemistry of Zn(II), Cd(II) and Hg(II) complexes with 1,2,4-triazole derivatives. *Dalton Trans.* 2011, *40*, 8475–8490.
11. Yan J. Z., Lu L. P. Syntheses, structures, and luminescence properties of two new open-framework zinc phosphites based on 1,2,4-triazole derivatives. *Chin. J. Struct. Chem.* 2018, *37*, 1331–1338.
12. Yan J. Z., Lu L. P., Feng S. S., Zhu M. L. Synthesis and structure of a ladder-like co-crystal CuICl with 3,5-dipropyl-4-amino-1,2,4-triazole. *Chin. J. Struct. Chem.* 2015, *34*, 401–407.
13. Chen X., Shang L., Cui H., Yang H., Liu L., Ren Y., Wang J. Four novel Zn(II)/Cu(II) coordination polymers containing hydroxyl groups: synthesis, crystal structure, luminescence sensing and photocatalysis properties. *CrystEngComm* 2020, *22*, 5900–5913.