Crystal structure of *catena*-[dodecaaqua(μ_3-benzene-1,3,5-tricarboxylato)-(μ_2-benzene-1,3,5-tricarboxylato)tricopper(II)], $Cu_3(H_2O)_{12}(C_9H_3O_6)_2$

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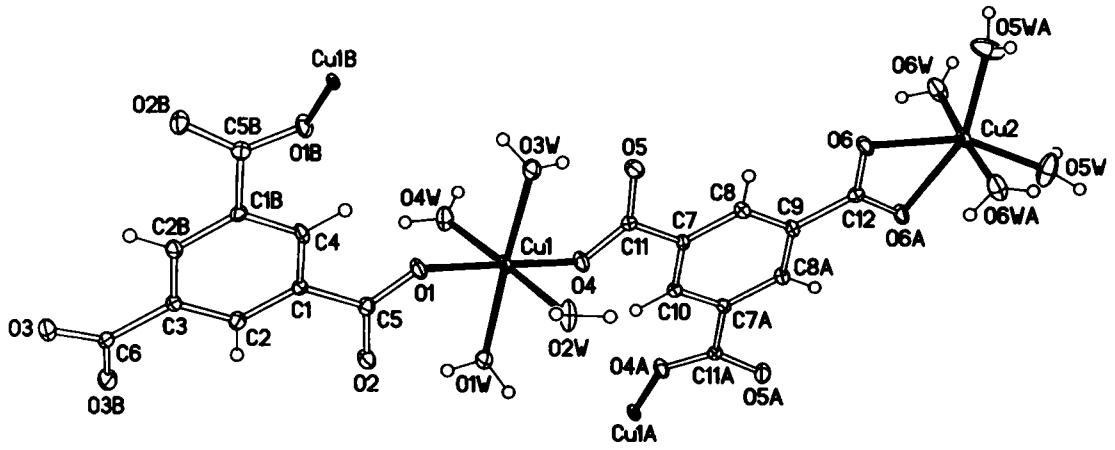

Abstract

$C_{18}H_{30}Cu_3O_{24}$, monoclinic, $C121$ (no. 5), a = 17.412(2) Å, b = 12.913(3) Å, c = 6.5669(1) Å, β = 111.93(2)°, V = 1369.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.083, T = 293 K.

Source of material

A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.186 g, 0.5 mmol), 1,3,5-benzenetricarboxylic acid (0.071 g, 0.3 mmol; H_3tma, tma = trimesate), Na_2CO_3 (0.055 g, 0.5 mmol) and water (10 ml) was sealed in a 15 ml Teflon-lined stainless steel reactor and heated to 433 K for 60 h. Blue crystals of $Cu_3(H_2O)_{12}(tma)_2$ suitable for X-ray analysis were obtained.

Experimental details

All H atoms were placed at calculated positions, and refined with isotropic displacement parameters using a riding model [d(C—H) = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C), d(O—H) = 0.82 Å and U_{iso}(H) = 1.2U_{eq}(O)].

Discussion

The crystal engineering of microporous polymers is currently of great interest owing to their intriguing topologies and potential applications in gas adsorption or storage, ion-exchange, heterogeneous catalysis [1]. The multi-functional ligand 1,3,5-benzenetricarboxylic acid was widely applied to construct microporous materials [2,3].

The X-ray analysis shows that the title crystal structure is composed of 1D zigzag chains, $[Cu_3(H_2O)_{12}(tma)_2]_n$. The two different Cu sites have coordination number of six and distorted octahedral environments. The tma ligands have two different binding modes. The hydrogen bonding interactions involving water molecules and carboxylate O atoms generates a three-dimensional framework. The title structure is isostructural with the reported structures of $[Co_3(H_2O)_{12}(tma)_2]_n$ [2,3] and $[Fe_3(H_2O)_{12}(tma)_2]_n$ [4].

Table 1. Data collection and handling.

Crystal:	blue prism, size 0.06 × 0.08 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.16 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5377, 2967
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2673
$N(param)_{refined}$:	208
Programs:	SHELXS-97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4c	0.2039	−0.0515	0.0258	0.029
H(2)	4c	0.1531	0.0128	−0.1184	0.029
H(3)	4c	0.2604	0.2249	−0.1044	0.042
H(4)	4c	0.3260	0.1636	−0.0428	0.042
H(5)	4c	0.3057	0.2593	0.4267	0.032
H(6)	4c	0.3652	0.2001	0.5599	0.032
H(7)	4c	0.2152	0.0715	0.5804	0.037
H(8)	4c	0.2466	−0.0181	0.5523	0.037
H(9)	4c	−0.1137	0.9438	−0.1552	0.062
H(10)	4c	−0.0880	0.9453	−0.3206	0.062
H(11)	4c	−0.0685	0.8681	0.3098	0.043
H(12)	4c	−0.0647	0.7672	0.2798	0.043
H(2A)	4c	0.3781	−0.2971	0.3227	0.023
H(4A)	2b	½	−0.0280	½	0.022
H(8A)	4c	0.1217	0.4934	0.1798	0.022
H(10A)	2a	0	0.2239	0	0.021

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*c*	0.25865(3)	0.10754(3)	0.23246(8)	0.0149(2)	0.0099(2)	0.0254(3)	0.0013(2)	0.0049(2)	0.0003(2)
Cu(2)	2*a*	0	0.81946(5)	0	0.0232(4)	0.0110(3)	0.0283(4)	0	0.0084(3)	0
O(1)	4*c*	0.3525(2)	0.0029(2)	0.3036(5)	0.020(2)	0.012(1)	0.035(2)	0.003(1)	0.004(1)	–0.003(1)
O(1W)	4*c*	0.1771(2)	0.0018(2)	0.0132(5)	0.023(2)	0.020(2)	0.024(2)	0.001(1)	0.003(1)	–0.000(1)
O(2)	4*c*	0.2852(2)	–0.1407(2)	0.1514(5)	0.016(2)	0.019(1)	0.035(2)	0.002(1)	–0.001(1)	–0.005(1)
O(2W)	4*c*	0.2792(2)	0.1703(2)	–0.0433(6)	0.029(2)	0.026(2)	0.055(2)	0.011(2)	0.022(2)	0.019(2)
O(3)	4*c*	0.5690(2)	–0.4791(2)	0.5719(6)	0.035(2)	0.017(2)	0.034(2)	0.005(1)	0.000(2)	–0.001(2)
O(3W)	4*c*	0.3418(2)	0.2179(2)	0.4316(5)	0.023(2)	0.022(2)	0.029(2)	0.004(1)	0.002(2)	0.000(1)
O(4)	4*c*	0.1575(2)	0.1996(2)	0.1703(6)	0.020(2)	0.014(1)	0.034(2)	0.003(1)	0.006(1)	–0.001(1)
O(4W)	4*c*	0.2344(2)	0.0403(2)	0.5023(5)	0.038(2)	0.023(2)	0.035(2)	0.007(1)	0.018(2)	0.010(1)
O(5)	4*c*	0.2159(2)	0.3449(2)	0.3420(5)	0.021(2)	0.022(2)	0.032(2)	0.003(1)	–0.000(1)	–0.006(1)
O(5W)	4*c*	–0.0829(2)	0.9154(3)	–0.2063(6)	0.064(3)	0.056(3)	0.049(2)	0.039(2)	0.039(2)	0.027(2)
O(6)	4*c*	0.0654(2)	0.6751(2)	0.1106(5)	0.021(2)	0.014(1)	0.035(2)	–0.005(1)	0.003(2)	–0.003(1)
O(6W)	4*c*	–0.0569(2)	0.8242(3)	0.2364(6)	0.049(2)	0.021(2)	0.048(2)	–0.003(2)	0.029(2)	–0.002(2)
C(1)	4*c*	0.4268(2)	–0.1539(3)	0.3932(7)	0.013(2)	0.016(2)	0.015(2)	0.002(1)	0.001(2)	–0.001(2)
C(2)	4*c*	0.4272(3)	–0.2613(4)	0.3940(7)	0.017(2)	0.017(2)	0.020(2)	–0.002(2)	0.005(2)	0.002(2)
C(3)	2*b*	½	–0.3162(4)	½	0.023(3)	0.013(3)	0.015(3)	0	0.004(3)	0
C(4)	2*b*	½	–0.1000(4)	½	0.026(3)	0.009(2)	0.024(3)	0	0.012(3)	0
C(5)	4*c*	0.3492(2)	–0.0933(3)	0.2766(6)	0.016(2)	0.019(2)	0.019(2)	0.002(2)	0.007(2)	0.001(2)
C(6)	2*b*	½	–0.4314(5)	½	0.029(3)	0.015(3)	0.015(3)	0	–0.001(3)	0
C(7)	4*c*	0.0738(3)	0.3496(3)	0.1048(7)	0.018(2)	0.013(2)	0.016(2)	0.002(1)	0.008(2)	0.002(2)
C(8)	4*c*	0.0730(3)	0.4571(3)	0.1066(7)	0.019(2)	0.016(2)	0.022(2)	–0.001(2)	0.008(2)	–0.002(2)
C(9)	2*a*	0	0.5106(4)	0	0.020(3)	0.012(2)	0.021(3)	0	0.011(2)	0
C(10)	2*a*	0	0.2960(4)	0	0.022(3)	0.015(3)	0.015(3)	0	0.006(2)	0
C(11)	4*c*	0.1549(3)	0.2940(3)	0.2143(6)	0.018(2)	0.016(2)	0.015(2)	–0.000(2)	0.004(2)	–0.001(2)
C(12)	2*a*	0	0.6261(4)	0	0.017(3)	0.020(3)	0.017(3)	0	0.003(2)	0

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