Crystal Structure of Catena-((μ_8 -benzene-1,2,4,5-tetracarboxylato)-triaqua-calcium(II)-copper(II))

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The structure of catena-((μ_8 -benzene-1,2,4,5-tetracarboxylato)-triaqua-calcium(II)-copper(II)) (**I**) was determined by X-ray crystallography. There is half of one benzene-1,2,4,5-tetracarboxylate tetra-anion (BTA^{4-}), each half Cu(II) and Ca(II) dications, and one and a half coordinated water molecules in its asymmetric unit. The compound crystallizes in the monoclinic $C2/c$ space group and was characterized as follows: $a = 14.1365(13)\text{\AA}$, $b = 13.2077(12)\text{\AA}$, $c = 8.8865(8)\text{\AA}$, $\beta = 126.365(3)^\circ$, $V = 1336.1(2)\text{\AA}^3$, $Z = 4$, $T = 150(2)\text{K}$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R_1 = 0.0779$ and $wR_2 = 0.1666$.

(Received April 16, 2019; Accepted May 16, 2019; Published on web August 10, 2019)

The construction of some metal-organic framework (MOF) based on alkaline earth metals and aromatic carboxylic acid has been emerging as a research field for more than thirty years.¹ The lack of d -orbital electrons in alkaline elements may result in even more coordination geometries in the construction of a MOF material.¹ However, by introducing both one transition and alkaline earth metals simultaneously into a MOF structure has been only reported recently.² The unsaturated coordination and weak coordinated solvent molecules around metal centers can provide some new type of potentially valuable MOF materials.³⁻⁶ Based on this design strategy, we have now prepared one Cu(II)-Ca(II) combined coordination complex (**I**) under the hydrothermal condition (Fig. 1). In (**I**), these two types of metals are bridged by benzene-1,2,4,5-tetracarboxylic acid (H_4BTA). Although no crystallographic void was detected in (**I**), it can adsorb N_2 gas to a certain extent. Herein, we will

report the crystal structure of (**I**).

In this research, compound (**I**) was prepared by dissolving $\text{Cu(NO}_3)_2 \cdot 2(\text{H}_2\text{O})$ (0.2 mmol, 48.0 mg), CaCl_2 (0.2 mmol, 23 mg) and H_4BTA acid (0.2 mmol, 51.0 mg) in 10 mL of water. The mixture was stirred for 10 min at ambient temperature and then heated in a 20-mL capacity Teflon-lined reaction vessel at 160°C for 3 days. After slowly cooling to room temperature at a rate of 5°C h^{-1} , the final plate-blue crystals (51.2 mg), suitable for X-ray structure analysis, could be obtained. The crystal and structure refinement data are summarized in Table 1.

Fig. 1 Chemical diagram of the title compound (**I**).

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Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{10}\text{H}_8\text{CaCuO}_{11}$	
Formula weight = 407.78	
$T = 150(2)$	
Crystal system: monoclinic	Space group: $C2/c$
$a = 14.1365(13)\text{\AA}$	
$b = 13.2077(12)\text{\AA}$	$\beta = 126.365(3)$
$c = 8.8865(8)\text{\AA}$	
$V = 1336.1(2)$	$Z = 4$
$D_x = 2.027\text{ g/cm}^3$	
Radiation: $\text{Mo K}\alpha$ ($\lambda = 0.71073\text{\AA}$)	
$\mu(\text{Mo K}\alpha) = 2.08\text{ mm}^{-1}$	$F(0\ 0\ 0) = 820.0$
Crystal size = $0.05 \times 0.05 \times 0.02\text{ mm}^3$	
No. of reflections collected = 5798	
No. of independent reflections = 1185	
θ range for data collection: 4.724 to 50°	
Data/Restrains/Parameters = $1185/6/106$	
R indices [$I \geq 2\sigma(I)$]: $R_1 = 0.0779$, $wR_2 = 0.1637$	
R indices (all data): $R_1 = 0.0840$, $wR_2 = 0.1666$	
Goodness-of-fit on $F^2 = 1.086$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.97\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -1.55\text{ e}\text{\AA}^{-3}$
Measurement: Bruker Smart APEX II CCD diffractometer	
Program system: SHELXTL	
Structure determination: intrinsic phasing (SHELXT-2014/410)	
Refinement: full matrix least-squares (SHELXL-2014/711)	
CCDC deposition number: 1900686

Fig. 2 Molecular structure of the title compound shown as 30% thermal probability. The symmetry codes in Fig. 2 meet those in Tables S1 and S2.

H atoms bonded to C atoms were positioned geometrically with $C-H = 0.93 \text{ \AA}$ (aromatic) and refined in a riding mode [$U_{iso}(H) = 1.2U_{eq}(\text{aromatic C})$]. H atoms bonded to water oxygen atoms were initially found in difference maps and refined with constraints of $d_{O-H} = 0.85(2) \text{ \AA}$ and $U_{iso}(H) = 1.5U_{eq}(O)$. In the final refinement, their positions were not satisfactorily converged and were then restrained. The relatively high R and wR values because of the bad diffraction quality of the slim crystal. Although we have tried our best several times to select better crystal samples for the X-ray diffraction experiment, we were unsuccessful each time. The highest peak of the residual electron density ($0.97 \text{ e \AA}^{-3}$) at $(0.0000 \ 0.0149 \ 0.7500)$ is $1.06 \text{ \AA}$ away from atom O6, and the deepest hole ($-1.55 \text{ e \AA}^{-3}$) at $(0.5000 \ 0.1979 \ 0.7500)$ is $1.47 \text{ \AA}$ away from atom H2, respectively.

The asymmetric unit of (**I**) was composed of half a benzene-1,2,4,5-tetracarboxylate tetra-anion (BTA^{4-}), each half a Cu(II) and Ca(II) dications both lying on a two-fold axis, and one and a half coordinated water molecules (Fig. 2). The two lateral carboxylate planes ($C4/O1/O2$ and $C5/O3/O4$) on the benzene group are twisted $60.7(1)^\circ$ away from each other. The Cu(II) center adopted a slightly distorted square-pyramidal coordination polyhedron ($\tau = 0.16$).⁷ Two carboxylate O1 oxygen atoms from the BTA^{4-} anion and two O5 water molecules constitute the base plane, and the water oxygen O6 atom resides on the vertex of the square-pyramid. The Cu(II) atom is *ca.* $0.11 \text{ \AA}$ above away from the base plane. The Cu–O_{base plane} bond lengths ($1.970(8) \text{ \AA}$ and $2.019(6) \text{ \AA}$) are significantly shorter than the vertical Cu–O6 bond ($2.248(13) \text{ \AA}$). This should be largely attributed to the spatial hindrance and the Jahn-Teller effect of the electron orbitals of the Cu(II) atom. Regarding the calcium atom, it was coordinated by three pairs of carboxylate oxygen atoms from six separated BTA^{4-} anions, resulting in a distorted octahedral environment. These Ca–O bond distances and O–Ca–O angles range from $2.267(7)$ to $2.328(7) \text{ \AA}$ and from $81.2(3)$ to $176.1(3)^\circ$, respectively (Table S1), which are comparable to some analogs.¹¹ Two adjacent Cu(II) and Ca(II) cations bridged by a $\mu_2\text{-COO}^-$ group is of $3.961(2) \text{ \AA}$ between them. Also two neighboring Ca(II) atoms linked by a carboxylate group are of $5.103(2) \text{ \AA}$ away from each other. As a whole, two Cu(II) and

six Ca(II) cations were linked by one BTA^{4-} anion, resulting an alternative array viewed along the $[001]$ axis.

In the crystal packing, a complex three-dimensional metal coordination network was formed, which was further consolidated by three O–H...O hydrogen bonds (Table S2). For a simplified topological understanding, the Cu(II), Ca(II) cations and BTA^{4-} anion in (**I**) has been regarded as being independent two-, six- and eight-connected nodes, respectively. Thus, the whole coordination network can be finally viewed as a 6,8-connected net with the Schläfli symbol of $\{3.4^{13}.6\} \{3^2.4^8.5^9.6^7.7^2\}$ by analysis of the program *TOPOS 4.0* (Fig. S1).⁸

To evaluate the adsorbability of compound (**I**), a N_2 gas adsorption experiment was performed at ambient temperature. Although no apparent crystallographic void was detected by an analysis of the program *PLATON*,⁹ the results indicate that compound (**I**) can efficiently adsorb N_2 gas to a certain extent under the tested condition with a BET surface area and Langmuir areas of *ca.* $63.0 \text{ m}^2 \text{ g}^{-1}$, $98.2 \text{ m}^2 \text{ g}^{-1}$, respectively (Fig. S2), and the pore volume in (**I**) is about $0.10 \text{ cm}^3 \text{ g}^{-1}$. The N_2 adsorption of (**I**) may be related to the release of the weak coordinating of water molecules in (**I**). Further research on the mechanism will be conducted in our lab.

Supporting Information

This material is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

Acknowledgements

This work is supported by the Ph. D. Programs Foundation of Hubei Minzu University (No. MY2015B012).

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