

## 杂-双核配合物 $[\text{CaCu}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_4]_n$ 的合成、 晶体结构及热稳定性

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## Synthesis, Crystal Structure and Thermal Stability of a Novel Hetero-bimetallic Complex: Bis(malonato)tetra-(aqua)calcium(II)copper(II)

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**Abstract:** The title complex,  $[\text{CaCu}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_4]_n$ , with a formula of  $\text{C}_6\text{H}_{12}\text{CaCuO}_{12}$  and  $M_r=379.78$  has been synthesized and characterized by single crystal X-ray diffraction structure analysis, elemental analysis, IR spectra and TG-DTG techniques. The results show that the crystal is Orthorhombic, space group  $Pb\bar{c}n$  with  $a=0.669\ 21(5)$  nm,  $b=1.370\ 23(5)$  nm,  $c=1.322\ 39(10)$  nm,  $V=1.212\ 59(16)$  nm<sup>3</sup>,  $D_c=2.080$  g·cm<sup>-3</sup>,  $\mu=2.288$  mm<sup>-1</sup>,  $F(000)=772$  and  $Z=4$ . The final  $R=0.054\ 0$  and  $wR=0.112\ 8$  for 1 189 observed reflections with  $I>2\sigma(I)$ . The structure of the title complex consists of  $\text{CaO}_8$  polyhedra and  $\text{CuO}_6$  elongated octahedra linked together by malonate ligands. The Ca(II) cation, on a twofold axis, is coordinated by two water molecules and six malonate O atoms. The Cu(II) cation, which lies in a centre of symmetry in an octahedral arrangement, is coordinated by four malonate O atoms and two water molecules. The structure comprises alternating layers along the  $[101]$  plane, with the shortest Cu···Cu distance of  $0.762\ 46(6)$  nm. The whole 3D structure is maintained and stabilized by the presence of hydrogen bonds. Its thermo gravimetric analysis was determined by TG-DTG techniques. CCDC: 663184.

**Key words:** calcium; copper; malonate; crystal structure; thermal stability

There has been considerable interest in the design and synthesis of transition metal complexes with carboxylate ligands in coordination chemistry, due to the fact that this type of complexes has potential applications in molecule-based magnets, catalysis,

supramolecular chemistry and biological systems<sup>[1-3]</sup>. As an important flexibility dicarboxylate ligand, malonate dianion contains two carboxylate groups located in the 1,3-position, so it can adopt monodentate, chelated bidentate and tridentate bridging conformational mode

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to form various 1D, 2D and 3D structures<sup>[4-7]</sup>. However, detailed structural data about hetero-bimetallic complexes are very limited, especially those involving alkaline-earth metals<sup>[8-14]</sup>. The complexes  $[\text{CaM}(\text{mal})_2(\text{H}_2\text{O})_4]$  ( $\text{M}$ =divalent transition metal;  $\text{mal}=\text{C}_3\text{H}_2\text{O}_4$ ) and  $[\text{CaNi}(\text{mal})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  were previously synthesized and reported by Gil de Muro et al.<sup>[15]</sup>. But only for the manganese and nickel complexes, their crystal structures have also been described<sup>[15]</sup>. We have reported the crystal structure of  $[\text{CaCo}(\text{mal})_2(\text{H}_2\text{O})_4]$  in our previous work<sup>[16]</sup>. In this paper, we describe the synthesis and crystal structure of the title complex,  $[\text{CaCu}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_4]_n$  (**1**), a novel Cu-Ca hetero-bimetallic malonate complex.

## 1 Experimental

### 1.1 Synthesis of $[\text{CaCu}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_4]_n$

$\text{Cu}(\text{OH})_2\text{CO}_3$  (0.220 g, 1 mmol) and  $\text{Ca}(\text{OH})_2$  (0.071 4 g, 1 mmol) were added slowly to an aqueous solution (20 mL) of malonic acid (0.312 g, 3 mmol); the reaction mixture was continuously stirred at 328 K for 2 h, cooled to room temperature and then filtered. Blue single crystals were obtained from the filtrate after one month. Yield, 35%. Anal. Calcd. (%). for  $\text{C}_6\text{H}_{12}\text{CaCuO}_{12}$ : C, 19.0; H, 3.2%. Found: C, 18.9; H, 3.1%. FTIR (KBr,  $\nu/\text{cm}^{-1}$ ): 3 558s, 3 217s, 2 921m, 1 593s, 1 456s, 1 378s, 1 286m, 1 181s, 967m, 942m, 826m, 750s, 588s.

### 1.2 Structure determination

A red single crystal with dimensions of 0.30 mm  $\times$  0.25 mm  $\times$  0.25 mm was selected for X-ray structure analysis. The data were collected on a Bruker Smart CCD diffractometer using a graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm) at 292(2) K. A total of 6 570 reflections were collected in the range of  $2.97^\circ < \theta < 26.00^\circ$  by using an  $\omega$  scan mode, of which 1 189 were unique with  $R_{\text{int}}=0.023\ 9$ . The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques with SHELX-97 program<sup>[17]</sup>. All H atoms were placed in the calculated positions, refined with fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms. All of the non-hydrogen atoms were refined by full-matrix least-squares techniques for 1 161 observed reflections with  $I > 2\sigma(I)$  to give the final  $R=0.054\ 0$ ,  $wR=0.112\ 8$  ( $w=1/[\sigma^2(F_o^2) + (0.000\ 0P)^2 + 10.683\ 5]$ , where  $P=(F_o^2 + 2F_c^2)/3$ ),  $S=1.255$  and  $(\Delta/\sigma)_{\text{max}}=0.000$ . The highest peak and deepest hole in the final difference Fourier map are 774 and  $-1\ 134\ \text{e} \cdot \text{nm}^{-3}$ , respectively. Geometrical calculations and molecular diagrams were obtained with program PLATON<sup>[18]</sup>. Crystal data and structure refinement for the title complex are listed in Table 1, and the selected geometric parameters are given in Table 2.

CCDC: 663184.

Table 1 Crystal data and structure refinement for complex 1

Empirical formula	$\text{C}_6\text{H}_{12}\text{CaCuO}_{12}$	Crystal size / mm	0.30 $\times$ 0.25 $\times$ 0.25
Formula weight	379.78	$\theta$ range for data collection / ( $^\circ$ )	2.97 to 26.00
Temperature / K	292(2)	Limiting indices	$-8 \leq h \leq 5$ , $-16 \leq k \leq 14$ , $-16 \leq l \leq 16$
Wavelength / nm	0.071 073	Reflections collected / unique ( $R_{\text{int}}$ )	6 570 / 1 189 (0.023 9)
Crystal system	Orthorhombic	$F(000)$	772
Space group	$Pbcn$	Refinement method	Full-matrix least-squares on $F^2$
$a$ / nm	0.669 21(5)	Data / restraints / parameters	1 189 / 6 / 105
$b$ / nm	1.370 23(5)	Goodness-of-fit on $F^2$	1.258
$c$ / nm	1.322 39(10)	Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.054\ 0$ , $wR_2=0.112\ 8$
$V$ / $\text{nm}^3$	1.212 59(16)	$R$ Indices (all data)	$R_1=0.054\ 8$ , $wR_2=0.113\ 1$
$Z$	4	Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	774 and $-1\ 134$
$D_c$ / ( $\text{g} \cdot \text{cm}^{-3}$ )	2.080		

Table 2 Selected geometric parameters (nm,  $^\circ$ ) for complex 1

Cu(1)-O(1)	0.195 7(3)	Ca(1)-O(2)	0.236 3(4)	C(1)-O(2)	0.124 2(6)
Cu(1)-O(1)#1	0.195 7(3)	Ca(1)-O(3)#3	0.272 0(3)	C(3)-O(3)	0.126 9(6)

Continued Table 1

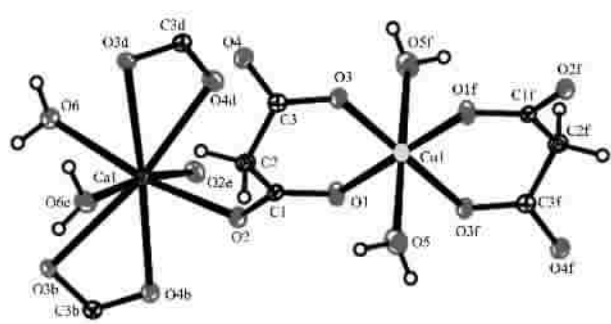
Cu(1)-O(5)	0.247 4(5)	Ca(1)-O(4)#3	0.244 7(4)	C(3)-O(4)	0.124 0(6)
Cu(1)-O(3)	0.193 9(3)	Ca(1)-O(6)	0.246 5(4)		
Cu(1)-O(3)#1	0.193 9(3)	C(1)-O(1)	0.126 8(6)		
O(1)-Cu(1)-O(1)#1	180.0(2)	O(3)#1-Cu(1)-O(3)	180.0(2)	O(4)-C(3)-O(3)	118.7(5)
O(2)-Ca(1)-O(2)#2	90.3(2)	O(3)-Cu(1)-O(5)	93.06(16)	O(6)#2-Ca(1)-O(6)	94.9(2)
O(2)-C(1)-O(1)	123.4(5)	O(3)#3-Ca(1)-O(4)#3	49.04(11)	Cu(1)-O(3)-Ca(1)#5	143.44(17)
O(3)-Cu(1)-O(1)	93.06(15)	O(4)#4-Ca(1)-O(3)#3	168.15(14)	C(1)-C(2)-C(3)	117.9(4)

Symmetry transformations used to generate the equivalent atoms: #1:  $-x+1, -y+1, -z$ ; #2:  $-x+2, y, -z+1/2$ ; #3:  $-x+3/2, -y+1/2, z+1/2$ ; #4:  $x+1/2, -y+1/2, -z$ ; #5:  $-x+3/2, -y+1/2, z-1/2$ .

## 2 Results and discussion

### 2.1 Structure description

The molecular structure of **1**, shown in Fig.1, can be described as a three-dimensional network of metal ions linked by hydrogen bonds. The Cu(II) ion located at the inversion centre is octahedrally coordinated by six oxygen atoms from two malonate groups (O(1) and O(3)) and two water molecules (O(5)). The Cu-O bond lengths are slightly different (0.195 7(3) and 0.193 9(3) nm for O(3) and O(1), respectively, 0.247 4(5) nm for O(5)). The Cu-O(5) were elongated by Jahn-Teller effect, and the Cu-O (mal) bonds are similar to the corresponding Cu-O bonds in  $[\text{Na}_2\text{Cu}(\text{mal})_2(\text{H}_2\text{O})_n]^{[19]}$  and  $[\text{MnCu}(\text{mal})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}^{[20]}$ . The angles of O(3)-Cu(1)-O(1) and O(5)-Cu(1)-O(5)#1 are  $93.06(15)^\circ$  and  $180.0(2)^\circ$ , respectively. The Ca(II) ion, which lies on a twofold axis in the structure, is eight-coordinated by two oxygen atoms (O(6)) from two water molecules and six oxygen atoms (O(2), O(3) and O(4)) from four malonate ligands, forming an irregular polyhedron. The Ca-O bond lengths are significantly different (0.236 3(4)~0.246 5(4) nm for O(2), O(4) and O(6); 0.272 0(3) nm for O(3)), longer than the corresponding ones in  $[\text{CaMn}(\text{mal})_2(\text{H}_2\text{O})_4]^{[15]}$  and  $[\text{CaNi}(\text{mal})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}^{[15]}$ . The bond angle of O(6)#2-Ca(1)-O(6) is  $94.9(2)^\circ$ . The other important bond angles O(2)-Ca(1)-O(2)#2 and O(4)#4-Ca(1)-O(3)#4 are  $90.3(2)^\circ$  and  $49.04(11)^\circ$ , respectively. As shown in Fig.1, the carboxylate groups of malonate ligand display different functionality: one carboxylate group (O(3), O(4)) adopts a 3-chelating bridging mode and the other one (O(1), O(2)) assumes a bidentate bridging mode to connect with two different metal centers (Ca(1), Cu(1)). The chelated six-membered malonate ring, Cu(1)-O(1)-C(2)-C(3)-C(1)-O(3), exhibits an envelop conformation in which only the methylene group is significantly shifted from the ring plane. The C-O bond lengths of carboxylate groups are in the range of 0.124 0(6)~0.126 9(6) nm, which are slightly shorter than the corresponding C-O bond in  $[\text{CaCo}(\text{mal})_2(\text{H}_2\text{O})_4]^{[16]}$ . The O-C-O bond angle for monodentate carboxylate group is  $123.4(5)^\circ$ , significantly larger than  $118.7(5)^\circ$  for the chelating one. The O(3) atoms in the title CaCu complex link the Cu and Ca ions (Cu(1)-O(3)-Ca(1)#5  $143.44(17)^\circ$ ) to form a zigzag chain extended along the b axis, and these chains are linked by malonate bridges generating a 2D network along the [101] plane (Fig.2), with the shortest Cu-Cu and Ca-Ca distances being 0.762 46(6) and 0.747 11(6) nm, respectively. It is interesting that the structure of **1** is similar to  $[\text{CaCo}(\text{mal})_2(\text{H}_2\text{O})_4]^{[16]}$ , but the crystal system and space group are quite different. Hydrogen bonding plays an important



Symmetry codes: a:  $3/2-x, 1/2-y, -1/2+z$ ; b:  $3/2-x, 1/2-y, 1/2+z$ ; c:  $-1/2+x, 1/2-y, -z$ ; d:  $1/2+x, 1/2-y, -z$ ; e:  $2-x, y, 1/2-z$ ; f:  $1-x, 1-y, -z$

Fig.1 Molecular structure of **1**, showing ellipsoids at the 30% probability level

ing an irregular polyhedron. The Ca-O bond lengths are significantly different (0.236 3(4)~0.246 5(4) nm for O(2), O(4) and O(6); 0.272 0(3) nm for O(3)), longer than the corresponding ones in  $[\text{CaMn}(\text{mal})_2(\text{H}_2\text{O})_4]^{[15]}$  and  $[\text{CaNi}(\text{mal})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}^{[15]}$ . The bond angle of O(6)#2-Ca(1)-O(6) is  $94.9(2)^\circ$ . The other important bond angles O(2)-Ca(1)-O(2)#2 and O(4)#4-Ca(1)-O(3)#4 are  $90.3(2)^\circ$  and  $49.04(11)^\circ$ , respectively. As shown in Fig.1, the carboxylate groups of malonate ligand display different functionality: one carboxylate group (O(3), O(4)) adopts a 3-chelating bridging mode and the other one (O(1), O(2)) assumes a bidentate bridging mode to connect with two different metal centers (Ca(1), Cu(1)). The chelated six-membered malonate ring, Cu(1)-O(1)-C(2)-C(3)-C(1)-O(3), exhibits an envelop conformation in which only the methylene group is significantly shifted from the ring plane. The C-O bond lengths of carboxylate groups are in the range of 0.124 0(6)~0.126 9(6) nm, which are slightly shorter than the corresponding C-O bond in  $[\text{CaCo}(\text{mal})_2(\text{H}_2\text{O})_4]^{[16]}$ . The O-C-O bond angle for monodentate carboxylate group is  $123.4(5)^\circ$ , significantly larger than  $118.7(5)^\circ$  for the chelating one. The O(3) atoms in the title CaCu complex link the Cu and Ca ions (Cu(1)-O(3)-Ca(1)#5  $143.44(17)^\circ$ ) to form a zigzag chain extended along the b axis, and these chains are linked by malonate bridges generating a 2D network along the [101] plane (Fig.2), with the shortest Cu-Cu and Ca-Ca distances being 0.762 46(6) and 0.747 11(6) nm, respectively. It is interesting that the structure of **1** is similar to  $[\text{CaCo}(\text{mal})_2(\text{H}_2\text{O})_4]^{[16]}$ , but the crystal system and space group are quite different. Hydrogen bonding plays an important

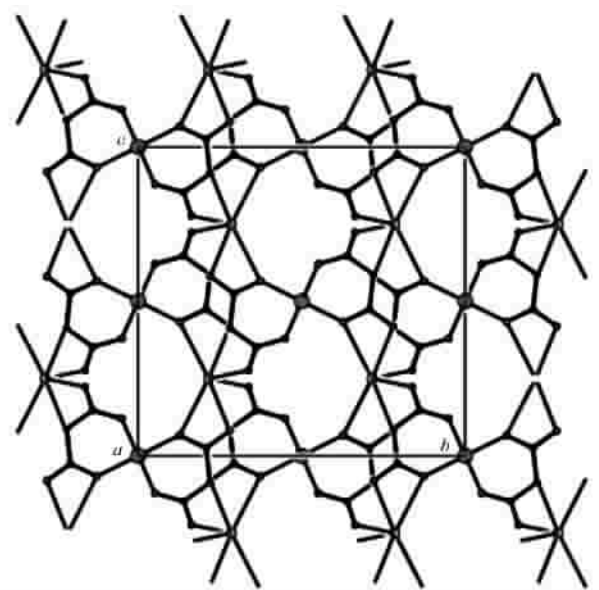
role in stabilizing the extended structure. Each coordinated water molecule bound to  $\text{Ca}(\text{II})$  and  $\text{Cu}(\text{II})$  ions is linked to the neighboring carboxylate oxygen atoms and other water molecule atoms through

hydrogen bonding interactions, and the whole 3D structure is maintained and stabilized by the presence of hydrogen bonds. The characteristics of the hydrogen bond network are given in Table 3.

Table 3 Hydrogen bond parameters for complex 1

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
$\text{O}(5)-\text{H}(5\text{A})\cdots\text{O}(4)\#6$	0.083(4)	0.200(4)	0.279 5(6)	160(7)
$\text{O}(5)-\text{H}(5\text{B})\cdots\text{O}(6)\#7$	0.079(3)	0.234(6)	0.290 9(6)	129(7)
$\text{O}(6)-\text{H}(6\text{A})\cdots\text{O}(1)\#8$	0.083(3)	0.196(4)	0.277 3(5)	166(7)
$\text{O}(6)-\text{H}(6\text{A})\cdots\text{O}(3)\#3$	0.083(3)	0.265(6)	0.305 9(6)	112(6)
$\text{O}(6)-\text{H}(6\text{B})\cdots\text{O}(5)\#9$	0.079(3)	0.215(4)	0.290 9(6)	163(7)

Symmetry transformations used to generate the equivalent atoms: #1:  $-x+1, -y+1, -z$ ; #2:  $-x+2, y, -z+1/2$ ; #3:  $-x+3/2, -y+1/2, z+1/2$ ; #4:  $x+1/2, -y+1/2, -z$ ; #5:  $-x+3/2, -y+1/2, z-1/2$ ; #6:  $x-1/2, -y+1/2, -z$ ; #7:  $-x+3/2, y+1/2, z$ ; #8:  $x+1/2, y-1/2, -z+1/2$ ; #9:  $-x+3/2, y-1/2, z$ .



Hydrogen atoms and water molecules were omitted for clarity

Fig.2 2D polymeric chains of 1 along the  $a$  axis

## 2.2 Thermal analysis

The results of TG (shown in Fig.3) illustrate that the compound decomposition takes place in three consecutive steps. The first stage mass loss is 18.10% between 130  $^\circ\text{C}$  and 185  $^\circ\text{C}$ , which coincides with the calculated value (19.31%) of four coordination water molecules. In the second stage, the release of malonate ligand occurs in the temperature range of 185~475  $^\circ\text{C}$  (loss weight 35.48%) with the theoretical value being 35.14%. The third stage (595~785  $^\circ\text{C}$ ) is inorganic residue formation, corresponding mass loss is 11.91% (theoretical value 11.71%) and the finally formation is

metal oxide.

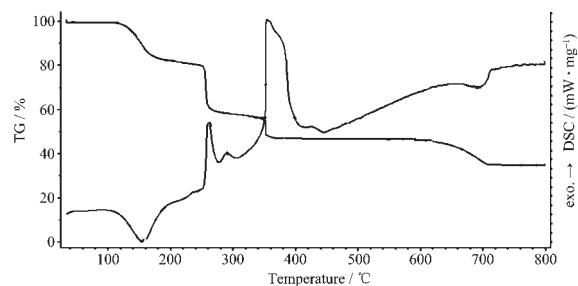


Fig.3 TG & DSC diagram showing the weight loss of 1

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