

## The Crystal Structure of Copper(II) Malonate Trihydrate

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The compound having an empirical formula  $\text{Cu}_8\text{C}_{24}\text{H}_{64}\text{O}_{56}$ , corresponding to copper(II) malonate trihydrate, is in fact the 2 : 1 co-crystal bis(diaquadimalonatocopper–tetraaquacopper)–[(diaquadimalonatocopper)–bis(tetraaquacopper)](2+) diaquadimalonatocuprate(2–),  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]_2 \cdot [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \{\text{Cu}(\text{H}_2\text{O})_4\}_2]^{2+} [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2]^{2-}$ . The compound crystallizes in the monoclinic  $P2_1/c$  space group, with  $a = 14.96(2)$ ,  $b = 14.97(2)$ ,  $c = 26.00(3)$  Å;  $\beta = 103.91(1)^\circ$ ;  $Z = 4$ ,  $\rho_{\text{calc}} = 2.064$  g cm<sup>-3</sup>.

*Key words:* crystal structure, coordination, copper, malonate, hydrogen bonding.

### INTRODUCTION

The interest in the structural chemistry of copper(II) malonate,  $\text{Cu}(\text{O}_2\text{C}-\text{CH}_2\text{CO}_2)$ , stems from the extensive use of the malonato ion in crystal engineering purposes.<sup>1</sup> Copper(II) malonate itself exists in several hydrated

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forms: copper(II) malonate dihydrate,  $[\text{H}_2\text{O} \cdot \text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_3]$  (space group  $Pcab$ )<sup>2</sup> (**1**), copper(II) malonate trihydrate,  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$  ( $Pbcn$ ) (**2**),<sup>3</sup> copper malonate tetrahydrate,  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_6]$  in  $(P\bar{1})^4$  (**3**) and another hydrate<sup>2</sup> having  $2^{5/6}$  water molecules per copper(II) malonate,  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4] \cdot [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \{\text{Cu}(\text{H}_2\text{O})_4\}_2]^{2+} [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2]^{2-}$  (**4**). A second trihydrate is monoclinic, but only the preliminary details ( $P2_1/n$ ,  $a = 10.62$ ,  $b = 21.00$ ,  $c = 13.50$  Å,  $\beta = 111^\circ$ )<sup>5</sup> have been published, and recently another monoclinic form was reported ( $C2/c$ ,  $a = 21.1219$ ,  $b = 21.1144$ ,  $c = 14.0149$  Å,  $\beta = 116.005^\circ$ ).<sup>6</sup> The structure of copper(II) hydrogenmalonate dihydrate is also known.<sup>7</sup> The reason for the variety of products from reaction between copper(II) salts and malonic acid is attributed to the conditions of the synthesis, the pH value, stoichiometry and temperature. Equally critical is the inherently low symmetry of the malonato dianion, which cannot, for example, pack across a center-of-inversion in solids. In our hands, the attempted synthesis of copper(II) hydrogen malonate yielded a compound whose empirical formulation is that of a trihydrate. The crystal structure of this compound,  $\text{Cu}_8\text{C}_{24}\text{H}_{64}\text{O}_{56}$  (**5**), is detailed here.

## EXPERIMENTAL

Well-defined deep-blue crystals were separated from an aqueous solution of copper carbonate and malonic acid (1:2 molar ratio) that had been kept at 5 °C for weeks. The room-temperature X-ray diffraction measurements on a  $0.25 \times 0.25 \times 0.20$  mm<sup>3</sup> crystal were performed on a MarResearch Image Plate detector diffractometer (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å); 95 frames were recorded at 2° intervals at counting time of 2 minutes.<sup>8</sup> The 19520 reflections were measured to  $2\theta = 52^\circ$  (collection range:  $0 \leq h \leq 18$ ,  $-18 \leq k \leq 18$ ,  $-32 \leq l \leq 30$ ), and these were averaged to 10898 ( $R_{\text{int}} = 0.074$ ) for solution by direct phase determination and refinement.<sup>9</sup> An empirical absorption<sup>10</sup> was applied to the model at convergence. Hydrogen atoms were located and refined with O–H fixed at  $0.85 \pm 0.01$  and  $\text{H} \cdots \text{H}$   $1.39 \pm 0.01$  Å; additionally, for each water molecule, the  $\text{Cu} \cdots \text{H}$  interactions were restrained to be equal by the SADI 0.01 instruction in SHELXL-97. The model converged to  $R = 0.078$  for 7471  $I \geq 2\sigma(I)$  reflections. The structure is depicted as 50% probability ORTEP<sup>11</sup> in the figure. Selected bond parameters are presented in Table I. The crystallographic-information-file has been deposited with the Cambridge Crystallographic Database Centre as CCDC 170695 (see Supplementary materials).

## RESULTS AND DISCUSSION

The crystal structure consists of two neutral diaquadimalonatecopper–tetraaquacopper units  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$ , co-existing with a diaqua-

TABLE I  
Selected bond lengths and angles in the coordination polyhedra

Bond lengths/Å		Bond angles/°	
Cu1–O11	1.951(5)	O11–Cu1–O13	91.7(2)
Cu1–O13	1.945(5)	O11–Cu1–O15	179.1(2)
Cu1–O15	1.952(5)	O11–Cu1–O17	89.0(2)
Cu1–O17	1.952(5)	O11–Cu1–O11w	90.8(3)
Cu1–O11w	2.410(7)	O11–Cu1–O12w	89.9(2)
Cu1–O12w	2.488(7)	O13–Cu1–O15	88.8(2)
		O13–Cu1–O17	179.3(2)
		O13–Cu1–O11w	90.9(3)
		O13–Cu1–O12w	89.1(3)
		O15–Cu1–O17	90.5(2)
		O15–Cu1–O11w	89.9(3)
		O15–Cu1–O12w	89.4(2)
		O17–Cu1–O11w	88.9(3)
		O17–Cu1–O12w	91.1(2)
		O11w–Cu1–O12w	179.3(3)
Cu2–O18	2.405(7)	O18–Cu2–O23w	97.4(3)
Cu2–O21w	1.925(6)	O18–Cu2–O21w	89.9(3)
Cu2–O22w	1.942(6)	O18–Cu2–O22w	92.4(3)
Cu2–O23w	1.944(6)	O18–Cu2–O24w	92.0(3)
Cu2–O24w	1.916(6)	O21w–Cu2–O22w	90.6(2)
		O21w–Cu2–O23w	172.6(3)
		O21w–Cu2–O24w	89.2(2)
		O22w–Cu2–O23w	90.4(2)
		O22w–Cu2–O24w	175.6(4)
		O23w–Cu2–O24w	89.1(2)
Cu3–O46	2.429(7)	O46–Cu3–O31w	97.0(3)
Cu3–O31w	1.929(6)	O46–Cu3–O32w	91.4(3)
Cu3–O32w	1.924(6)	O46–Cu3–O34w	92.0(3)
Cu3–O33w	1.916(6)	O46–Cu3–O33w	90.9(3)
Cu3–O34w	1.939(6)	O31w–Cu3–O32w	89.3(2)
		O31w–Cu3–O33w	172.0(3)
		O31w–Cu3–O34w	91.2(2)
		O32w–Cu3–O33w	89.1(3)

continued

TABLE I (cont.)

Bond lengths/Å		Bond angles/°	
		O33w–Cu3–O34w	90.0(3)
		O32w–Cu3–O34w	176.5(3)
Cu4–O41	1.952(5)	O41–Cu4–O43	91.7(2)
Cu4–O43	1.954(5)	O41–Cu4–O45	179.7(2)
Cu4–O45	1.967(5)	O41–Cu4–O47	88.9(2)
Cu4–O47	1.946(5)	O41–Cu4–O41w	90.2(3)
Cu4–O41w	2.504(8)	O41–Cu4–O42w	89.0(3)
Cu4–O42w	2.500(8)	O43–Cu4–O45	88.5(2)
		O43–Cu4–O47	179.3(2)
		O43–Cu4–O41w	90.6(3)
		O43–Cu4–O42w	89.9(3)
		O45–Cu4–O47	90.9(2)
		O45–Cu4–O41w	89.8(2)
		O45–Cu4–O42w	91.0(3)
		O47–Cu4–O41w	89.6(3)
		O47–Cu4–O42w	89.9(3)
		O41w–Cu4–O42w	179.1(2)
Cu5–O44	2.397(7)	O52w–Cu5–O53w	90.6(3)
Cu5–O51w	1.935(6)	O52w–Cu5–O54w	177.6(3)
Cu5–O52w	1.915(6)	O53w–Cu5–O54w	88.4(2)
Cu5–O53w	1.924(6)	O52w–Cu5–O51w	90.6(2)
Cu5–O54w	1.924(5)	O53w–Cu5–O51w	169.9(3)
		O54w–Cu5–O51w	89.9(2)
		O44–Cu5–O51w	96.0(3)
		O44–Cu5–O52w	91.9(3)
		O44–Cu5–O53w	93.9(3)
		O44–Cu5–O54w	90.4(3)
Cu6–O76	2.379(7)	O76–Cu6–O61w	93.3(3)
Cu6–O61w	1.939(6)	O76–Cu6–O62w	91.2(3)
Cu6–O62w	1.933(6)	O76–Cu6–O63w	95.8(3)
Cu6–O63w	1.938(5)	O76–Cu6–O64w	92.7(3)
Cu6–O64w	1.923(6)	O61w–Cu6–O62w	88.3(2)
		O61w–Cu6–O63w	170.8(3)
		O61w–Cu6–O64w	90.2(2)

continued

TABLE I (cont.)

Bond lengths/Å		Bond angles/°	
		O62w–Cu6–O63w	90.3(2)
		O62w–Cu6–O64w	175.9(3)
		O63w–Cu6–O64w	90.6(2)
Cu7–O71	1.956(5)	O71–Cu7–O73	92.2(2)
Cu7–O73	1.949(5)	O71–Cu7–O75	88.3(2)
Cu7–O75	1.952(5)	O71–Cu7–O77	179.0(2)
Cu7–O77	1.948(5)	O71–Cu7–O71w	91.6(3)
Cu7–O71w	2.416(7)	O71–Cu7–O72w	89.6(2)
Cu7–O72w	2.495(7)	O73–Cu7–O75	179.3(2)
		O73–Cu7–O77	88.8(2)
		O73–Cu7–O71w	90.9(3)
		O73–Cu7–O72w	89.4(3)
		O75–Cu7–O77	90.8(2)
		O75–Cu7–O71w	88.6(3)
		O75–Cu7–O72w	91.1(3)
		O77–Cu7–O71w	88.3(3)
		O77–Cu7–O72w	90.5(2)
		O71w–Cu7–O72w	178.8(2)
Cu8–O81	1.953(6)	O81–Cu8–O83	91.0(2)
Cu8–O83	1.949(5)	O81–Cu8–O85	180.0(3)
Cu8–O85	1.947(5)	O81–Cu8–O87	88.8(2)
Cu8–O87	1.949(6)	O81–Cu8–O81w	92.1(3)
Cu8–O81w	2.396(7)	O81–Cu8–O82w	88.1(3)
Cu8–O82w	2.413(8)	O83–Cu8–O85	89.0(2)
		O83–Cu8–O87	179.0(2)
		O83–Cu8–O81w	92.1(3)
		O83–Cu8–O82w	88.5(3)
		O85–Cu8–O87	91.1(2)
		O85–Cu8–O81w	87.9(3)
		O85–Cu8–O82w	92.0(3)
		O87–Cu8–O81w	88.9(3)
		O87–Cu8–O82w	90.5(3)
		O81w–Cu8–O82w	179.4(3)

dimalonatocopper–bis(tetraaquacopper) diaquadimalonatocuprate,  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \{\text{Cu}(\text{H}_2\text{O})_4\}_2] [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2]$  ion-pair (Figure 1). The four entities are connected by a three-dimensional network of hydrogen bonds. All water molecules are engaged in coordination to the copper atoms, and there are no lattice water molecules. The hydrogen bonds are formed between the water molecules and the oxygen acceptors of different malonato units. Of the 32 oxygen atoms belonging to the 8 malonato groups, their single-bond carboxyl oxygen atoms form each hydrogen bond with a water molecule. On the other hand, each of the double-bond carboxyl oxygen atoms forms two hydrogen bonds to a pair of water molecules. The present simple system consisted of single proton donor and acceptor types, therefore, represents an illustrative example for the better proton-accepting properties of the uncoordinated carboxylate ends with two available lone pair sites over the coordinated ones which tend to accept the hydrogen from a single water molecule. Every water molecule forms two hydrogen bonds, so that there are 48 independent hydrogen bonds (Table II) in a narrow range of  $\text{Ow}\cdots\text{O}$  distances from 2.567(8) (O34w $\cdots$ O88f, symmetry code:  $f = 1 - x, 2 - y, 1 - z$ ) to 2.99(1) Å (O82w $\cdots$ O76r, symmetry code:  $r = x, 1 + y, z$ ). Compound **5** differs from compound **4** in having an additional neutral  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$  entity. The asymmetry in the delocalized negative charge of the monodentate carboxyl groups generally induces shortening of the uncoordinated and lengthening of the coordinated C–O bonds from the respective bidentate values (Table III).

The extra  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$  unit in compound **5** only marginally increases the density compared with that of compound **4** (from 2.025 g cm<sup>-3</sup> to 2.064 g cm<sup>-3</sup>). However, compound **5** represents the largest structural diversity among aquamalonatocopper building blocks that have been described in the literature. It comprises a mononuclear anion, two crystallographically non-equivalent binuclear diaquadimalonatocopper–tetraaquacopper units and a trinuclear cationic entity. Malonato-bridged binuclear blocks also occur in compounds **1**, **2** and **3**; water molecules (1–4 or 6) complete the coordination polyhedra.

The mononuclear diaquadimalonatocopper anion (Figure 1d) features *trans*-octahedral coordination with four nearly identical equatorial Cu–O and two tetragonally elongated Cu–Ow interactions. The chelating malonato ligand binds in an envelope conformation, with the bite angle of approximately 91° (see Table I).

In the pair of binuclear neutral  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$  units (Figures 1a and 1c), Cu1 and Cu7 are also octahedrally coordinated, but only one *trans*-malonate is solely bidentate; the other bidentate malonate acts also as *anti-syn* bridge to the five-coordinated Cu2 and Cu6. The equa-

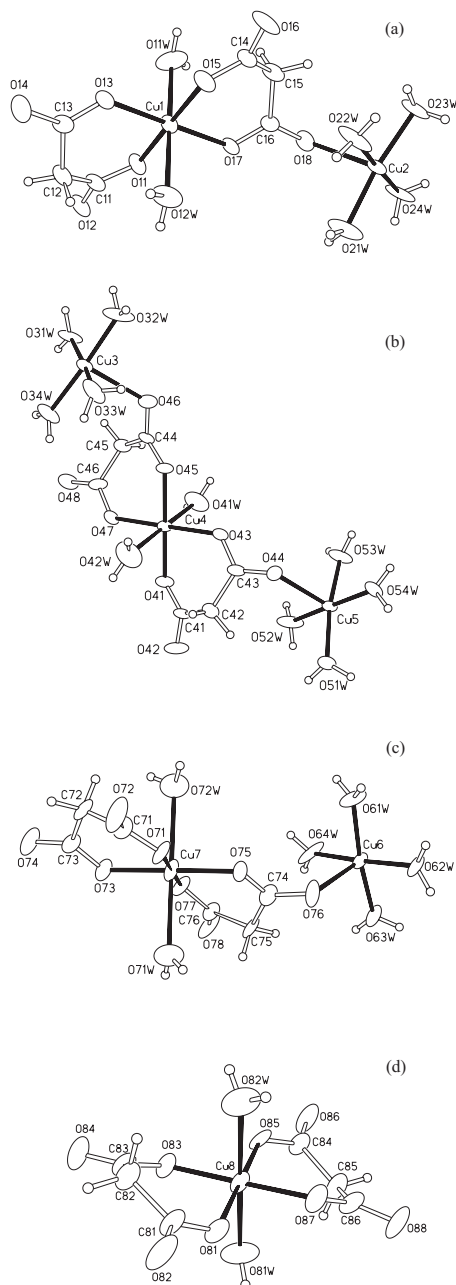


Figure 1. ORTEP of one of the two neutral  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$  entities (a); of the cationic  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \{\text{Cu}(\text{H}_2\text{O})_4\}_2]^{2+}$  entity (b); of the second neutral  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]$  entity (c); of the anionic  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2]^{2-}$  entity (d).

TABLE II  
Hydrogen bonds<sup>a</sup>

D–H...A	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\angle(\text{DHA})/^\circ$
O11w–H111...O88#1	2.803(9)	166(4)
O11w–H112...O46#2	2.926(9)	170(7)
O12w–H121...O42#3	2.794(9)	159(6)
O12w–H122...O84#4	2.880(9)	168(7)
O21w–H211...O18#5	2.681(8)	155(9)
O21w–H212...O81#6	2.672(8)	157(9)
O22w–H221...O71#7	2.687(8)	159(9)
O22w–H222...O82#6	2.605(8)	161(8)
O23w–H232...O72#7	2.635(8)	151(6)
O24w–H241...O42#8	2.652(8)	161(9)
O24w–H242...O17#5	2.715(8)	163(10)
O31w–H311...O12#5	2.636(8)	166(10)
O31w–H312...O47#8	2.748(8)	175(9)
O32w–H321...O75#7	2.701(8)	172(8)
O32w–H322...O48#8	2.645(8)	161(9)
O33w–H331...O76#7	2.685(8)	167(9)
O33w–H332...O87#6	2.683(8)	154(9)
O34w–H341...O11#5	2.715(8)	159(10)
O34w–H342...O88#6	2.567(8)	169(9)
O41w–H411...O16#9	2.791(9)	162(3)
O41w–H412...O72#10	2.86(1)	164(6)
O42w–H421...O12#11	2.88(1)	165(3)
O42w–H422...O78#3	2.777(9)	159(7)
O51w–H511...O84#12	2.643(8)	167(4)
O51w–H512...O15#13	2.707(8)	157(9)
O52w–H521...O74#12	2.628(8)	166(8)
O52w–H522...O83#12	2.665(8)	155(10)
O53w–H531...O44#7	2.694(8)	177(5)
O53w–H532...O73#12	2.714(8)	176(3)
O54w–H541...O43#7	2.738(8)	176(3)
O54w–H542...O16#13	2.627(8)	163(8)
O61w–H611...O13#13	2.706(8)	163(10)
O61w–H612...O46#7	2.704(8)	173(9)
O62w–H621...O45#7	2.716(8)	159(10)

continued



TABLE II (cont.)

D-H...A	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\langle(\text{DHA})^\circ$
O62w-H622...O78#12	2.626(8)	148(10)
O63w-H631...O86#12	2.637(8)	162(10)
O63w-H632...O77#12	2.702(8)	175(9)
O64w-H641...O85#12	2.671(8)	159(10)
O64w-H642...O14#13	2.625(8)	165(10)
O71w-H711...O44#11	2.988(9)	156(9)
O71w-H712...O82#14	2.762(9)	148(9)
O72w-H721...O48#15	2.788(9)	166(6)
O72w-H722...O86	2.84(1)	165(8)
O81w-H811...O74	2.795(9)	157(5)
O81w-H812...O18#16	2.910(9)	151(9)
O82w-H821...O14#17	2.79(1)	146(7)
O82w-H822...O76#18	2.99(1)	146(9)

<sup>a</sup> H atoms were fixed with D-H at  $(0.85 \pm 0.01) \text{\AA}$  and H...H at  $(1.39 \pm 0.01) \text{\AA}$

<sup>b</sup> Symmetry transformations used to generate equivalent atoms:

- #1  $x-1, y-1, z-1$  #2  $x, -y+1/2, z-1/2$  #3  $x, -y+3/2, z-1/2$ ;  
 #4  $x, y-1, z-1$  #5  $-x, -y+1, -z$  #6  $-x+1, -y+2, -z+1$ ;  
 #7  $-x+1, -y+1, -z+1$  #8  $-x, y-1/2, -z+1/2$  #9  $x, -y+1/2, z+1/2$ ;  
 #10  $x-1, -y+3/2, z-1/2$  #11  $x, -y+3/2, z+1/2$  #12  $-x+1, y-1/2, -z+3/2$ ;  
 #13  $-x+1, y+1/2, -z+1/2$  #14  $x, y-1, z$  #15  $x+1, -y+3/2, z+1/2$ ;  
 #16  $x+1, y+1, z+1$  #17  $x, y+1, z+1$  #18  $x, y+1, z$ .

torial plane around Cu1 and Cu7 (with a negligible distortion) consists of nearly equally distant carboxylate oxygen atoms, with two apical water molecules completing the octahedron. The bridged metals Cu2 and Cu6 in the two independent units, comprise nearly regular square-pyramidal coordination, with four water molecules at the base and longer bond to the bridging malonate. The same coordination pattern was previously reported in the crystal of the isolated moiety **2**,<sup>3</sup> obtained from a warm aqueous mixture of basic copper(II) carbonate and malonic acid. The neutral binuclear moiety is also included in the structure of **4**,<sup>2</sup> showing that the solid-state copper malonate structures can be formally constructed by combining the known coordination building blocks acting as inorganic supramolecular synthons.

In the trinuclear cation  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \{\text{Cu}(\text{H}_2\text{O})_4\}_2]^{2+}$  (Figure 1b), two structurally independent tetraquacopper(II) squares (Cu3 and Cu5) are bridged by the central octahedral diaquadimalonatocopper(II) unit. The fifth oxygen coordination site of the terminal square-pyramidal copper atoms is donated by one of the free carbonyl groups of the bidentate malona-

TABLE III  
 Characteristic carbon-oxygen distances ( $d/\text{\AA}$ ) in the carboxylate groups

	Coordination mode		
	Monodentate	Bidentate	Non-coordinated
Maximum	1.290(9) C14–O15	1.269(9) C16–O17	1.288(9) C73–O73
Minimum	1.24(1) C73–O74	1.247(9) C44–O46	1.22(1) C46–O48
Average	1.274	1.261	1.243

tes, which now each serves as a monodentate bridge through O44 and O46. In this sense, the cation can be derived from the neutral diaquadimalonato-copper-tetraaquacopper entity by adding a tetraaquacopper(II) unit, while by removing such a unit the diaquadimalonatecopper(II) dianion may be derived. The basal Cu–O bonds for Cu3 and Cu5 reveal a significant distortion in both pyramids towards a trigonal bipyramidal geometry.<sup>12</sup> The angles between the adjacent bonds around Cu3 and Cu5 are close to 90°. The central copper atom in a similar trinuclear cationic unit in **4** lacks a water molecule, and the metal atom is situated in a square pyramidal surrounding.<sup>2</sup> Another difference with **1** is also reflected in the absence of a mirror plane through the atom Cu4 (due to the orientation of the pyramidal copper centers).

*Supplementary materials.* – CCDC 170695 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))

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## SAŽETAK

### Kristalna struktura bakrova(II) malonata trihidrata

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Utvrđeno je da je spoj s empirijskom formulom  $\text{Cu}_8\text{C}_{24}\text{H}_{64}\text{O}_{56}$ , koja odgovara bakrovu(II) malonatu trihidratu, zapravo 2 : 1 ko-kristal, tj. bis(diakvadimalonatobakar–tetraakvabakar)–[(diakvadimalonatobakar)–(bis(tetraakvabakar))]<sup>(2+)</sup> diakvadimalonatokuprat(2–):  $[(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \text{Cu}(\text{H}_2\text{O})_4]_2 \cdot [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2 \cdot \{\text{Cu}(\text{H}_2\text{O})_4\}_2]^{2+} [(\text{H}_2\text{O})_2\text{Cu}(\text{O}_2\text{CCH}_2\text{CO}_2)_2]^{2-}$ . Taj spoj kristalizira u monoklinskoj prostornoj grupi  $P2_1/c$ ,  $a = 14,96(2)$ ,  $b = 14,97(2)$ ,  $c = 26,00(3)$  Å;  $\beta = 103,91(1)^\circ$ ;  $Z = 4$ ,  $\rho_{\text{calc}} = 2,064$  g cm<sup>-3</sup>.