Journal of Molecular Structure 1064 (2014) 122–129

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Copper(II) benzoate dimers coordinated by different linear alcohols – A systematic study of crystal structures

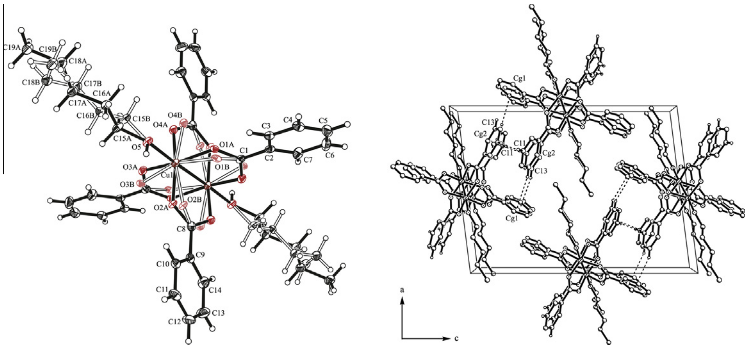
Felix Katzsch [a], Alexander S. Münch [b], Florian O.R.L. Mertens [b],*, Edwin Weber [a],*

[a] Institute of Organic Chemistry, Technical University Bergakademie Freiberg, Leipziger Straße 29, 09596 Freiberg, Germany
[b] Institute of Physical Chemistry, Technical University Bergakademie Freiberg, Leipziger Straße 29, 09596 Freiberg, Germany

HIGHLIGHTS

- Three new alcohol coordinated copper(II) benzoate paddle wheels have been prepared.
- The structures of the compounds are determined by single crystal X-ray diffraction.
- The structures with different alcohols have been investigated by a systematic study.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 December 2013
Received in revised form 21 January 2014
Accepted 21 January 2014
Available online 4 February 2014

Keywords:
Copper(II) benzoates
Paddle-wheel unit
Alcohol coordination
Crystal structure
Supramolecular interactions

ABSTRACT

Three new copper(II) benzoates coordinated by 1-propanol, $[Cu_2(PhCOO)_4(1\text{-}PrOH)_2]$ $[Cu_2(PhCOO)_4(H_2O)_2]$ (**3**), 1-butanol, $[Cu_2(PhCOO)_4(1\text{-}BuOH)_2]$ (**4**) and 1-pentanol, $[Cu_2(PhCOO)_4(1\text{-}PentOH)_2]$ (**5**) at the available metal coordination sites, have been prepared and investigated with reference to their X-ray crystal structures. In all cases, dimeric paddle-wheel complexes where two copper(II) ions are held together by four benzoates were found. Moreover, the complexes show 1-propanol and water (**3**), 1-butanol (**4**) and 1-pentanol (**5**) coordinated to the free coordination sites of the Cu(II) ions. The dimeric complex units are connected with each other by strong O—H···O hydrogen bonds to form strands linked together via weaker C—H···O and C—H···π interactions. Comparative discussion including the redetermined crystal structures obtained from copper(II) benzoate in the presence of methanol (**1**) or ethanol (**2**) allows to draw argumentation regarding the coordination of linear alcohols in corresponding crystals of paddle-wheel complexes.

1. Introduction

Copper carboxylates are a well-known and rather broadly investigated group of carboxylates occurring in a variety of structures with different properties and applicability dependent on the basicity of the ligands, steric factors, hydrogen bonds, concentration and ratio of the starting compound in the reaction solution and the used solvent [1]. Chen et al. gave a survey of possible binding patterns between copper ions and carboxylates [2] (Fig. 1). According to this, there is a basic distinction between a mono-atomic (**I**) [3,4] and a tri-atomic bridging mode of the carboxylate with reference to the metal ions. The tri-atomic binding pattern can further be specified as *syn-syn* (**II**) [5], *anti-anti* (**III**) [6,7], or

---

* Corresponding authors. Tel.: +49 (0)3731 39 3192; fax: +49 (0)3731 39 3588 (F.O.R.L. Mertens). Tel.: +49 (0)3731 39 2386; fax: +49 (0)3731 39 3170 (E. Weber).

E-mail addresses: florian.mertens@chemie.tu-freiberg.de (F.O.R.L. Mertens), edwin.weber@chemie.tu-freiberg.de (E. Weber).

http://dx.doi.org/10.1016/j.molstruc.2014.01.080
0022-2860/© 2014 Elsevier B.V. All rights reserved.

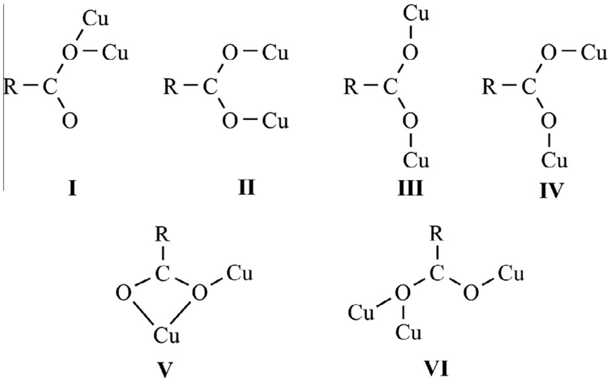


Fig. 1. Binding relations between a carboxylate group and copper ions.

syn-anti (**IV**) [8–11] conformations as well as a mode including a mono- and bi-dentate conformation (**V**) [12,13]. Moreover, a bridging scheme containing not only mono-atomic but also tri-atomic *syn-anti* and *anti-anti* types (**VI**) has been described [2] and it was shown in the literature that the mono- and tri-atomic *syn-syn* conformations allow the formation of dinuclear complexes while the *syn-anti* and the *anti-anti* geometry generally favor layer or chain structures [14,15].

The *syn-syn* conformation in **II** is perhaps the most interesting mode of binding owing to the dimeric molecular structure element existing in the well investigated copper(II) acetate monohydrate [16–18]. This contains a so-called paddle-wheel dimeric unit in which four acetato ligands bridge two copper(II) ions at the four equatorial coordination positions in a *syn-syn* way. The two free coordination sites of the metal ions can be occupied by different Lewis basic secondary ligands, like water molecules in the case of copper(II) acetate monohydrate. In the solid state, these dimers are linked together by intermolecular hydrogen bonds between the oxygen atoms of the bridging acetates and the water molecules [18,19]. By maintaining the paddle-wheel structure, the acetate groups can be replaced by other carboxylates, such as derived from benzoic acid [19–21] or benzene-1,3,5-tricarboxylic acid, in the latter case giving rise to a three-dimensional porous lattice of the metal–organic framework HKUST-1 [22,23]. Actually, the copper(II) paddle-wheel structures involving benzoates as carboxylate units are an intensively investigated group of substances with regard to magnetic [24–26] and electronic properties [27]. The secondary ligand molecules attached to the unsaturated coordination sites of the copper(II) ions can be very different resulting in various applications including the use as antiarthritic agent [28], non-steroidal anti-inflammatory [29], antitumor drug [30] or antibacterial [31] and fungicidally active compounds [32,1] of the copper(II) benzoate type dependent on the coordinated species. In particular the secondary ligands refer to Lewis bases containing oxygen donors, like ethanol [33] or benzoic acid [34] and nitrogen donors such as *N*,*N*-dimethylformamide [35], different pyridines [36,1,37] and quinolones [34].

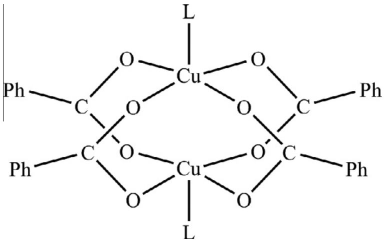


Fig. 2. Paddle-wheel structure motif of the copper(II) benzoate dimers aimed at in this paper (L = alcohol).

In view of the importance of this class of substances considering the influence of the secondary coordinated species, we aimed at structurally studying a systematic series of respective crystalline compounds. They feature the basic structure motif as specified in Fig. 2 with the coordinated ligands L representing different alcohols that may exercise specific influences on intermolecular interactions and packing modes. It is also intended to find a procedure for preparation of the compounds with the most possible uniformity.

2. Experimental

All denoted chemicals are commercially available and were used without further purification.

2.1. Preparation of compounds

Solutions of benzoic acid (367 mg, 3 mmol) in 25 mL of the respective alcohols (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) were added to copper(II) acetate monohydrate (300 mg, 1.5 mmol)) in 25 mL deionized water. The obtained light blue precipitates were separated from the liquid phase and washed twice with the corresponding solvent (10 mL). In the cases of methanol, ethanol and 1-propanol, the alcohol water mixtures were slowly evaporated. Because of the poor miscibility of 1-butanol and 1-pentanol in water, only the organic phases were used for evaporation. The transparent blue-green crystals of compounds **1**–**5**, respectively, obtained in each case were found to be suitable for single crystal X-ray investigation. Chemical compositions of the respective crystals are derived from the single crystal X-ray study, giving rise to compound formulas for complexes **1**–**5** as specified in Table 1.

2.2. X-ray structure determination

The single crystal X-ray diffraction data of the studied compounds were collected at 100 K on a Bruker Kappa diffractometer equipped with an APEX II CCD area detector and graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) employing φ and ω scan modes. The data were corrected for Lorentz and polarization effects. Semiempirical absorption correction was applied using the SADABS program [38]. The SAINT program [38] was used for the integration of the diffraction profiles. The crystal structures were solved by direct methods using SHELXS-97 [39] and refined by full-matrix least-squares refinement against F^2 using SHELXL-97 [39]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms. Geometrical calculations were performed using PLATON [40] and molecular graphics were generated using SHELXTL [39].

3. Results and discussion

3.1. Synthesis

As originally intended, we aimed at studying the structures of a systematic series of copper(II) benzoate paddle wheel compounds

Table 1
Specification of complexes involved in this study.

Alcohol used	Formula of obtained compounds (composition of complex)
Methanol (MeOH)	$[Cu_2(PhCOO)_4(PhCOOH)_2]$ (**1**)
Ethanol (EtOH)	$[Cu_2(PhCOO)_4(EtOH)_2]$ (**2**)
1-Propanol (1-PrOH)	$[Cu_2(PhCOO)_4(1\text{-PrOH})_2]\cdot[Cu_2(PhCOO)_4(H_2O)_2]$ (**3**)
1-Butanol (1-BuOH)	$[Cu_2(PhCOO)_4(1\text{-BuOH})_2]$ (**4**)
1-Pentanol (1-PentOH)	$[Cu_2(PhCOO)_4(1\text{-PentOH})_2]$ (**5**)

Table 2
Crystal data and refinement details of the structure determination.

Compound	**3**	**4**	**5**
Empirical formula	$Cu_4C_{62}H_{60}O_{20}$	$Cu_2C_{36}H_{40}O_{10}$	$Cu_2C_{38}H_{44}O_{10}$
Formula weight	1379.30 g mol^{-1}	759.76 g mol^{-1}	787.81 g mol^{-1}
Temperature	100(2) K	100(2) K	100(2) K
Crystal system	triclinic	triclinic	monoclinic
Space group	*P-1*	*P-1*	$P2_1/n$
Unit cell dimensions	a = 10.2682(4) Å b = 10.5743(4) Å c = 14.1678(5) Å α = 102.774(2)° β = 97.473(2)° γ = 98.756(2)°	a = 6.5393(2) Å b = 14.1201(5) Å c = 19.2519(7) Å α = 83.597(2)° β = 89.630(2)° γ = 87.881(2)°	a = 14.4378(5) Å b = 6.5518(2) Å c = 19.4732(8) Å α = 90° β = 97.236(2)° γ = 90°
Volume, *Z*	1461.22(9) Å^3, 1	1765.33(10) Å^3, 2	1827.37(11) Å^3, 2
Density (calculated)	1.567 g cm^{-3}	1.429 g cm^{-3}	1.432 g cm^{-3}
Adsorption coefficient	1.514 mm^{-1}	1.260 mm^{-1}	1.220 mm^{-1}
F(000)	708	788	820
Crystal size (in nm)	0.36 × 0.17 × 0.15	0.39 × 0.16 × 0.07	0.51 × 0.13 × 0.05
Radiation, wavelength	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
θ range for data collection	1.50–25.00	1.06–25.00	2.84–25.00
Reflections collected	27067	31756	12614
Unique data, R_{int}	5144, 0.022	6205, 0.041	3211, 0.033
Index ranges $\pm h \pm k \pm l$	−12/12, −12/12, −16/16	−7/5, −16/16, −22/22	−17/17, −7/7, −23/18
Max. and min transmission	0.8047 and 0.6118	0.9170 and 0.6392	0.9415 and 0.5750
Refinement method	Full-matrix least square on F^2	Full-matrix least square on F^2	Full-matrix least square on F^2
Data/restraints/parameters	5144/16/404	6205/65/540	3211/52/268
Goodness-of-fit on F^2	1.041	1.117	1.042
R_1, wR_2 [$I > 2\sigma(I)$]	0.0260, 0.0660	0.0516, 0.1239	0.0325, 0.0693
R_1, wR_2 (all data)	0.0274, 0.0668	0.0637, 0.1281	0.0439, 0.0720
Max. and av. shift/error	0.001, 0.000	0.000, 0.000	0.000, 0.000
Min. and max. resid. dens.	−0.842 eÅ^{-3}, 1.041 eÅ^{-3}	−0.599 eÅ^{-3}, 1.586 eÅ^{-3}	−0.495 eÅ^{-3}, 0.364 eÅ^{-3}

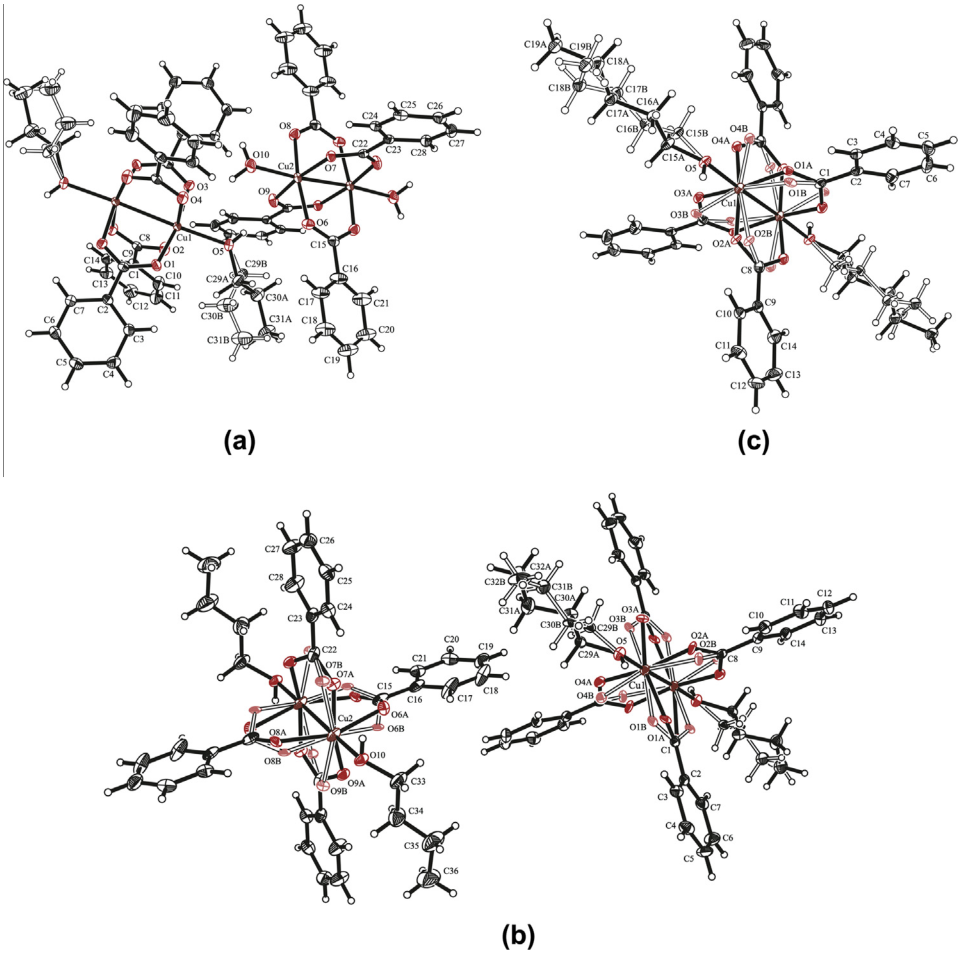


Fig. 3. Molecular structures of **3** (a), **4** (b) and **5** (c), showing the atom labeling scheme with displacement ellipsoids drawn at the 50% probability level.

involving the whole range of alcohols from methanol to 1-pentanol as secondary coordinated species. However, using the present experimental conditions, this could not be realized in all cases (Table 1).

Unlike the expectation, the blue green crystalls of **1** obtained from slow evaporation of the methanol–water phase were found to contain dimeric copper(II) benzoate units having benzoic acid molecules coordinated to the open metal sites of copper(II) instead of two methanols. The respective crystal structure is a known one and has already been described by Kawata et al. [34]. Following an analogous experimental procedure with a mixture of ethanol and water, the desired coordination of ethanol molecules is formed, giving rise to a compound (**2**) the crystal structure of which is also known from recent literature [33]. Crystallization of copper(II) benzoate from 1-propanol-water results in the formation of a complex **3** composed of two different copper(II) benzoate paddle wheel units. One, as expected, being secondarily coordinated to two 1-propanol molecules while the other one includes two molecules of water at the open metal sites. Finally, in the cases of 1-butanol and 1-pentanol, complexes **4** and **5** containing only the respective alcohols coordinated to the copper(II) ions were obtained. Hence, though a rather uniform method of preparation was used, complexes of different composition (**1**–**5**) have been isolated.

3.2. X-ray single crystal structure analysis

As mentioned above, structures of two of the isolated complexes (**1** and **2**) have already been reported in the literature and can directly serve for structural comparison, while the complexes **3**–**5** and thus also their X-ray crystal structures are new. These are described and comparatively discussed including relevant data of the known structures in the following.

Crystal data and details of the structure determinations involving the new compounds are given in Table 2. Compounds **3** and **4** crystallize in the triclinic space group *P-1*, crystals of **5** are monoclinic $P2_1/n$. The asymmetric part of the unit cell of **3** contains two half paddle wheels with a water molecule and a 1-propanol molecule at the open metal sites, respectively. The 1-propanol shows twofold disorder with a site occupancy factor (*sof*) of 0.71 (Fig. 3a). Also in the structure of **4**, two half molecules are found in the asymmetric part of the unit cell, however with two 1-butanol molecules positioned at the free copper sites with different orientations (Fig. 3b). One of the solvent molecules is elongated away from the paddle wheel and is also twofold disordered (*sof* = 0.51), like in the case of 1-propanol, while the other one is bent at the alcoholic oxygen. By way of contrast, the asymmetric part of the unit cell of **5** consists of only a half paddle wheel with an elongated 1-pentanol molecule at the copper showing again a twofold disorder (*sof* = 0.83) (Fig. 3c). Moreover, the paddle wheel frameworks of **4** and **5** are disordered by torsion of the carboxylate group regarding the connection to the copper atoms. This differs from the regular structure **3** containing nearly rectangular O—Cu—O angles (Table 3). The site occupancy factors for each carboxylate disorder are 0.51 (O1A, O3A), 0.50 (O2A, O4A), 0.53 (O6A, O8A), 0.52 (O7A, O9A) and 0.52 (O1A, O3A), 0.50 (O2A, O4A) for **4** and **5**, respectively. As a result, during the structure refinement of **3**, **4** and **5** it was necessary to use DELU, SIMU, ISOR and EADP restrains to conform the anisotropic displacement parameters of the carboxylate oxygens O1A, O4B, O7A, O7B, O8B (**4**) and O1A, O2B, O4A (**5**) as well as of the alcohol carbons C32A, C32B (**4**) and C15B, C16B, C18B, C19B (**5**).

Comparison of the Cu—Cu distances within the paddle wheels shows a slight decrease with growing size of the alcohol (Table 4). Considering the literature known copper(II) benzoate paddle wheels, though being predominantly coordinated by nitrogen containing ligands, it is obvious that the present structures **3**–**5** as well as the ethanol coordinated paddle wheel of **2** [33] feature shorter Cu—Cu distances. Only in a structure having coordinated 1,4-dioxane, the Cu—Cu distance is somewhat shorter (2.569 Å) [41]. On the other site, the longest Cu—Cu distance (*d* = 2.694 Å) is found in the copper(II) benzoate with 6-methylquinoline as ligands [42]. Moreover, the Cu—O distances at the open metal sites of **3**–**5** are shorter than in the literature structures, excepting the pyridine N-oxide coordinated copper(II) benzoate which is comparable in this property (*d* = 2.134 Å) [43].

In the packing structures of the paddle wheel units of **3**–**5**, hydrogen bonding interactions (Table 5) are dominant. In a more detailed description, in the structure of **3**, the paddle wheels

Table 4
Cu—Cu and Cu—O distances of **3**, **4** and **5**.

	Distances (Å)		
	3	**4**	**5**
Cu1—Cu1	2.589	2.572	2.571
Cu2—Cu2	2.597	2.579	
Cu1—O5	2.126 (1-PrOH)	2.133 (1-BuOH)	2.126 (1-PentOH)
Cu2—O10	2.173 (H_2O)	2.131 (1-BuOH)	

Table 3
O—Cu—O bond angles of **3**, **4** and **5**.

	Angles (°), (atoms)		
	3	**4**	**5**
Molecule 1 Disorder site A	89.82 (O1—Cu1—O2) 90.11 (O2—Cu1—O3) 87.52 (O3—Cu1—O4) 90.67 (O4—Cu1—O1)	88.26 (O1A—Cu1—O2A) 75.43 (O2A—Cu1—O3A) 89.84 (O3A—Cu1—O4A) 104.31 (O4A—Cu1—O1A)	102.69 (O1A—Cu1—O2A) 90.81 (O2A—Cu1—O3A) 72.90 (O3A—Cu1—O4A) 91.31 (O4A—Cu1—O1A)
Molecule 1 Disorder site B		89.49 (O1B—Cu1—O2B) 104.30 (O2B—Cu1—O3B 90.77 (O3B—Cu1—O4B) 72.76 (O4B—Cu1—O1B)	75.19 (O1B—Cu1—O2B) 85.98 (O2B—Cu1—O3B) 109.01 (O3B—Cu1—O4B) 87.72 (O4B—Cu1—O1B)
Molecule 2 Disorder site A	89.78 (O6—Cu2—O7) 89.63 (O7—Cu2—O8) 90.53 (O8—Cu2—O9) 88.18 (O9—Cu2—O6)	73.67 (O6A—Cu2—O7A) 88.43 (O7A—Cu2—O8A) 106.84 (O8A—Cu2—O9A) 88.21 (O9A—Cu2—O6A)	
Molecule 2 Disorder site B		105.97 (O6B—Cu2—O7B) 90.89 (O7B—Cu2—O8B) 69.83 (O8B—Cu2—O9B) 90.64 (O9B—Cu2—O6B)	

Table 5
Selected intermolecular hydrogen bond type contacts of the studied compounds.

Atoms involved	Symmetry	Distance (Å)		Angle (°)
		D···A	H···A	D—H···A
3				
O5—H5A···O9	*x*, *y*, *z*	2.837	1.99	173
O10—H10A···O4	−*x*, 1−*y*, 1−*z*	2.887	2.05	164
C20—H20···O7	1 + *x*, *y*, *z*	3.423	2.57	150
O26—H26···O6	−*x*, 2−*y*, −*z*	3.399	2.65	136
O28—H28···O3	−*x*, 1−*y*, −*z*	3.384	2.45	167
C29A—H29A···O1	*x*, *y*, *z*	3.291	2.67	121
C30B—H30C···O1	*x*, *y*, *z*	3.288	2.60	127
C31A—H31A···Cg1[a]	1−*x*, 1−*y*, 1−*z*	3.675	2.89	138
C31A—H31C···Cg3[b]	*x*, *y*, *z*	3.604	2.77	143
4				
O5—H5A···O1A	1−*x*, 1−*y*, 1−*z*	2.820	2.36	115
O5—H5A···O2A	1−*x*, 1−*y*, 1−*z*	3.180	2.41	153
O5—H5A···O2B	1−*x*, 1−*y*, 1−*z*	2.790	2.00	158
O10—H10A···O8A	2−*x*, −*y*, −*z*	2.757	2.00	150
O10—H10A···O8B	2−*x*, −*y*, −*z*	3.229	2.47	151
C3—H3···O2A	1−*x*, 1−*y*, 1−*z*	3.520	2.61	160
C10—H10···O1B	1−*x*, 1−*y*, 1−*z*	3.420	2.47	177
C21—H21···O7A	−1 + *x*, *y*, *z*	3.521	2.58	172
C24—H24···O8B	2−*x*, −*y*, −*z*	3.440	2.56	155
C34—H34B···O9A	*x*, *y*, *z*	3.267	2.46	138
C34—H34B···O9B	*x*, *y*, *z*	3.368	2.71	124
C25—H25···Cg1[a]	1 + *x*, −1 + *y*, *z*	3.457	2.70	137
C27—H27···Cg2[c]	1−*x*, −*y*, 1−*z*	3.492	2.57	164
C30A—H30B···Cg1[a]	1−*x*, 1−*y*, 1−*z*	3.730	2.84	149
C34—H34A···Cg4[d]	2−*x*, −*y*, −*z*	3.762	2.80	165
5				
O5—H5A···O1A	1−*x*, 2−*y*, −*z*	3.228	2.43	167
O5—H5A···O1B	1−*x*, 2−*y*, −*z*	2.799	1.99	167
O5—H5A···O2B	1−*x*, 2−*y*, −*z*	2.823	2.51	104
C3—H3···O2A	1−*x*, 2−*y*, −*z*	3.348	2.43	168
C10—H10···O1A	1−*x*, 2−*y*, −*z*	3.561	2.66	164
C15B—H15C···O3A	*x*, *y*, *z*	3.290	2.67	122
C11—H11···Cg2[c]	3/2−*x*, 1/2 + *y*, 1/2−*z*	3.621	2.89	136
C13—H13···Cg1[a]	1/2 + *x*, 3/2−*y*, 1/2 + *z*	3.729	2.91	148
C16A—H16A···Cg3[e]	1−*x*, 2−*y*, −*z*	3.596	2.78	143

[a] Cg1 is defined as the center of the ring with C2—C7.
[b] Cg3 is defined as the center of the ring with C16—C21.
[c] Cg2 is defined as the center of the ring with C9—C14.
[d] Cg4 is defined as the center of the ring with C23—C28.
[e] Cg3 is defined as the center of the bond between C9 and C14.

coordinated with water and 1-propanol molecules are alternately arranged forming a strand along the crystallographic *c*-axis (Fig. 4). The packing is stabilized by strong O—H···O hydrogen bonds [44,45] between the alcoholic hydroxyl group and a carboxylate oxygen [d(O5···O9) = 2.8373(17) Å] as well as between the water hydroxyl group and a carboxylate oxygen [d(O10···O4) = 2.8869(18) Å]. In addition, weak C—H···O interactions [46,47] [d(C28···O3) = 3.384(2) Å] involving an aromatic C—H group and a carboxylate oxygen as well as weak C—H···π contacts [48–50] [d(C31A···Cg3) = 3.603(3) Å] between the methyl group of the 1-propanol and an aromatic ring of a water coordinated paddle wheel are present within the strand. The strands are linked together by weak C—H···O type hydrogen bonds [d(C20···O7) = 3.423(2) Å, d(C26···O6) = 3.39982 Å] and weak C—H···π contacts [d(C31A···Cg1) = 3.669(4) Å]. Due to the disorder of the 1-propanol molecule, C31A—H31C···Cg3 and C31A—H31A···Cg1 contacts exist only to 71% in the structure. Furthermore, two additional intramolecular C—H···O interactions [d(C29A···O1) = 3.290 Å (71%) and d(C30B···O1) = 3.288 Å (29%)] are present alternately depending on the corresponding disorder site.

The paddle-wheel units of **4** are arranged in two different strands along the crystallographic *a*-axis as result of the different orientation of the coordinated 1-butanol molecules (elongated and bent) (Fig. 5). The intermolecular interactions including carboxylate groups depend on the corresponding disorder sites with the interactions being involved in the structure only to around 50%. Stabilization of the strands is accomplished by strong O—H···O bonds between an alcoholic hydroxyl group and a carboxylate oxygen as well as by weak C—H···O contacts involving an aromatic C—H group and a carboxylate oxygen. Moreover, an intra-complex C—H···O contact between a methylene group of 1-butanol and a carboxylate oxygen occurs in equal parts as C34—H34B···O9A [d(C34···O9A) = 3.267(8) Å] or as C34—H34B···O9B [d(C34···O9B) = 3.368(9) Å]. The different strands are connected among one another by weak C—H···π contacts [d(C25···Cg1) = 3.457(4) Å, d(C27···Cg2) = 3.492(5) Å, d(C30A···Cg1) = 3.73(3) Å, d(C34···Cg4) = 3.762(6) Å] (Fig. 6) and van-der-Waals interactions between butyl alcohols of adjacent paddle wheels give rise to additional stabilization of the structure.

As contrasted with **4**, in the structure **5** of the 1-pentanol coordinated paddle-wheel complex, strands composed of only

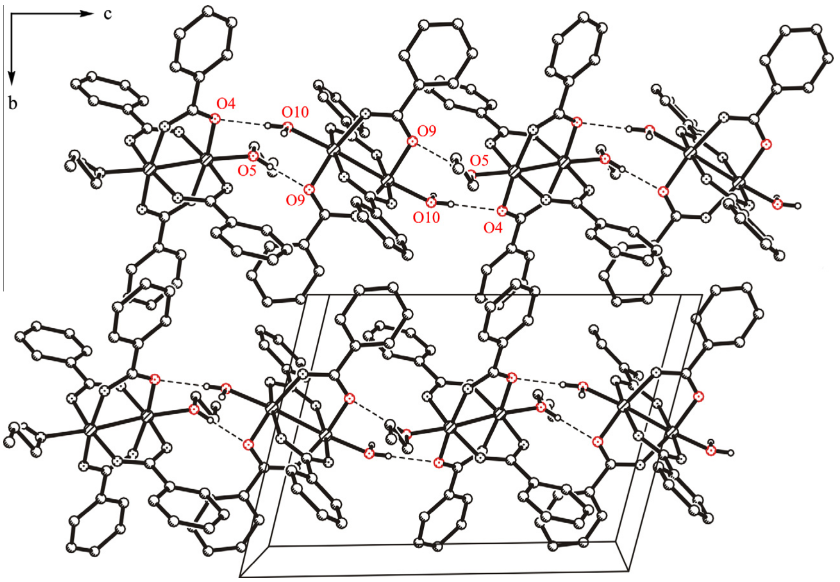


Fig. 4. Paddle wheel strands within the packing scheme of **3** including O—H···O bonds. Non-relevant hydrogen atoms are omitted for clarity.

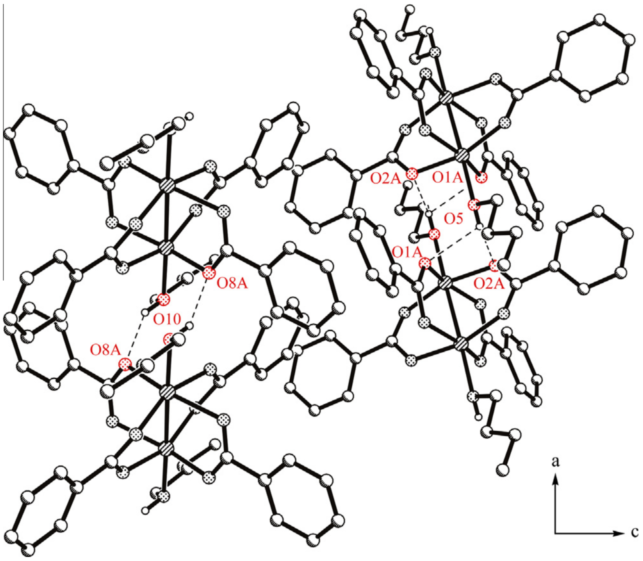


Fig. 5. Two types of paddle wheel strands within the structure of **4** showing strong O—H···O bonds. Only one disorder site is shown. Non-relevant hydrogen atoms are omitted for clarity.

one conformational paddle wheel type are formed running in the direction of the crystallographic *b*-axis (Fig. 7). But analogous to the 1-butanol structure, the intermolecular interactions occur only to around 50% in the structure owing to the conformational disorder sites of the carboxylate groups. Therefore, the stabilization of the strands is also supported by strong O—H···O bonds between an alcohol hydroxyl group and a carboxylate oxygen as well as by weak C—H···O contacts present in both disorder sites. To around 83%, the C—H···π contact C16A—H16A···Cg3 [d(C16A···Cg3) = 3.596(4) Å] of a 1-pentanol methylene group and a bond of an aromatic ring additionally stabilize the strands.

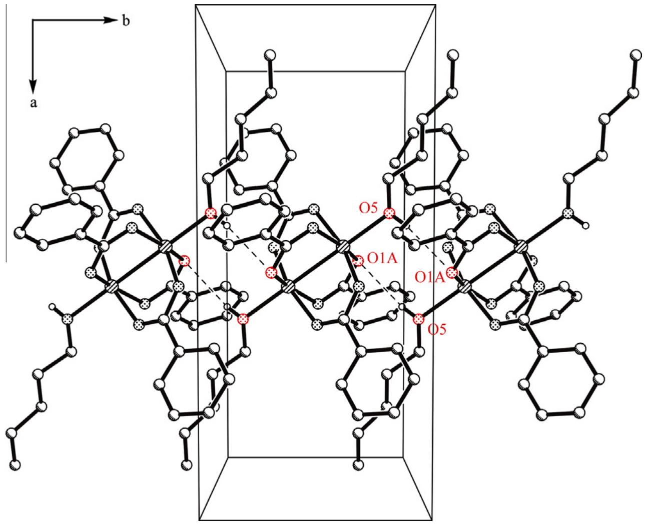


Fig. 7. Strand of the 1-pentanol coordinated paddle wheels in structure **5** including strong O—H···O bonds between them. Only one disorder site is shown. Non-relevant hydrogen atoms are omitted for clarity.

Furthermore an intra-complex C—H···O contact C15B—H15C···O3A exists between a methylene group of the disordered 1-pentanol and a carboxylate oxygen [d(C15B···O3A) = 3.29(2) Å] to only 9% due to the two independent disorders. Interconnection of the strands is arranged by the weak C—H···π contacts C11—H11···Cg2 [d(C11···Cg2) = 3.621(3) Å] and C13—H13···Cg1 [d(C13···Cg1) = 3.729(3) Å] (Fig. 8). Similar to the structure **4**, van-der-Waals interactions between adjacent 1-pentanol chains also occur here.

In comparison of the copper(II) benzoate paddle wheels coordinated with ethanol (**2**) [33], 1-propanol (**3**), 1-butanol (**4**) and 1-pentanol (**5**), it is obvious that the coordinated alcohol molecules at the open metal sites have a significant influence on the

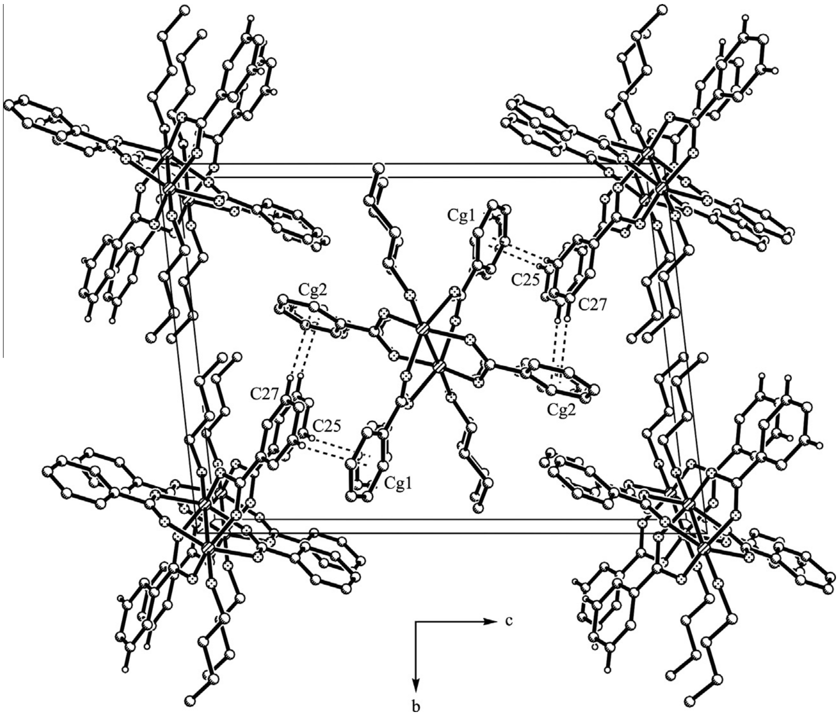


Fig. 6. Intermolecular C—H···π interactions between the paddle wheels in structure **4**. Only one disorder site is shown. Non-relevant hydrogen atoms are omitted for clarity.

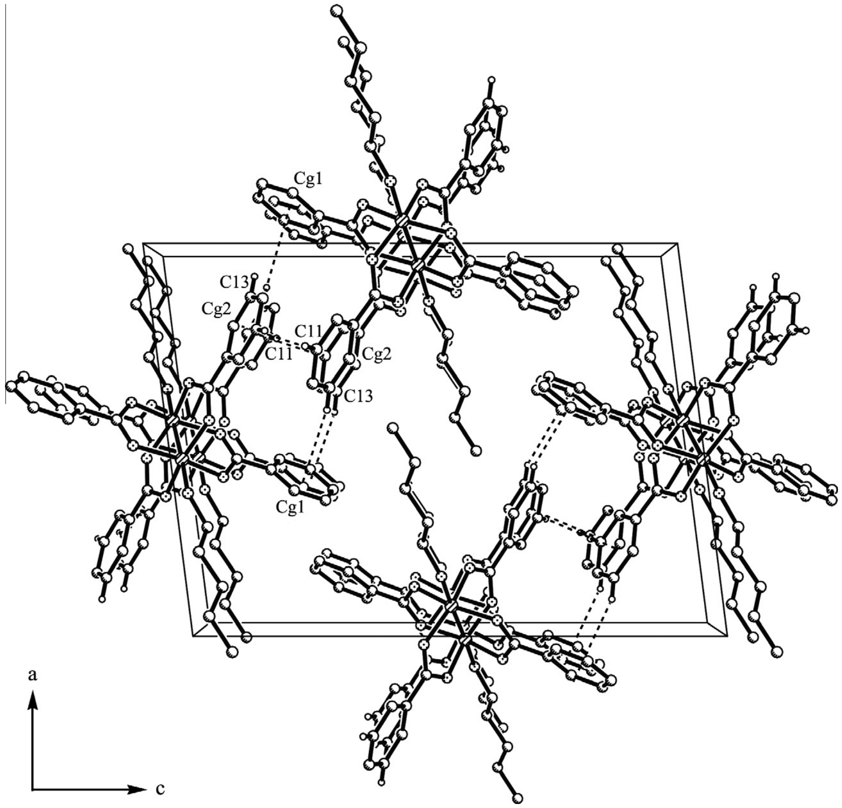


Fig. 8. Intermolecular C—H···π interactions between the paddle wheels in structure **5**. Only one disorder site is shown. Non-relevant hydrogen atoms are omitted for clarity.

arrangement of the crystal packing. Due to the bulkiness of the paddle wheel, the formation of a close packing is hindered. This, however, can be moderated in a different way. For instance, as shown in the crystal structures of **2** [33] and **4**, two paddle wheels in the asymmetric unit possessing alcohols of different orientations, considering the alkyl chains, are used. In both these structures, one solvent molecule is elongated while the other one is bent. In the case of 1-propanol, a water molecule is coordinated on the open metal site of a second paddle wheel to form a stable structure. Only 1-pentanol seems to fully meet the requirement for the arrangement of a stable packing, being expressed by the fact that one single paddle wheel coordinated by an elongated alcohol molecule is sufficient for the structure formation. These findings may also explain why the formation of a stable complex using the small alcohol molecule methanol proved unsuccessful under the given experimental conditions but yielded **1**.

4. Conclusion

Three new copper(II) benzoate paddle wheels coordinated with 1-propanol (**3**), 1-butanol (**4**) and 1-pentanol (**5**) at the open metal sites, respectively, have been synthesized by a precipitation reaction and a following slow evaporation of the residual solution. The compounds were identified by single crystal X-ray analysis and investigated regarding their crystal packing motifs and intermolecular interactions. In the crystalline state, all three structures consist of paddle wheel strands stabilized by strong O—H···O hydrogen bonds and being connected among one another by weaker C—H···O and C—H···π contacts. Owing to the use of alcohol molecules of different lengths, the structures show variable arrangements featuring the inclusion of water to the copper sites and different orientations of the alcohol alkyl chains.

In some way, the results of this study could make a contribution to more deeply understand the potential behavior of secondary building units regarding solvent coordination of metal–organic frameworks (MOFs).

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft (Priority Program 1362 “Porous Metal-Organic Frameworks”, A.M., F.M. and E.W.) as well as the Ministry of Science and Art of Saxony (Cluster of Excellence “Structure Design of Novel High-Performance Materials via Atomic Design and Defect Engineering [ADDE]”) together with the European Union (European Regional Development Fund, F.K. and E.W.) for financial support.

Appendix A. Supplementary material

CCDC-955889 (**3**), CCDC-955890 (**4**) and CCDC-955891 (**5**) contain the supplementary crystallographic data for this article. This data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.01.080.

References

[1] B. Kozlevčar, N. Lah, D. Žlindra, I. Leban, P. Šegedin, Acta Chim. Slov. 48 (2001) 363.
[2] Z.N. Chen, S.X. Liu, J. Qui, Z.M. Wang, J.L. Huang, W.X. Tang, J. Chem. Soc., Dalton Trans. 20 (1994) 2989.
[3] P.Y. Boukari, A. Busnot, F. Busnot, A. Leclaire, M.A. Bernard, Acta Cryst. B38 (1982) 2458.
[4] J.-P. Costes, F. Dahan, J.-P. Laurent, Inorg. Chem. 24 (1985) 1018.
[5] M. Kato, Y. Muto, Coord. Chem. Rev. 92 (1988) 45.
[6] M. Inoue, M. Kubo, Inorg. Chem. 9 (1970) 2310.
[7] R. Kiriyama, H. Ibamoto, K. Matsuo, Acta Cryst. 7 (1954) 482.
[8] P.K. Coughlin, S.J. Lippard, J. Am. Chem. Soc. 106 (1984) 2328.

[9] E. Colacio, J.-M. Dominguez-Vera, J.-P. Costes, R. Kivekäs, J.-P. Laurent, J. Ruiz, M. Sundberg, Inorg. Chem. 31 (1992) 774.
[10] G.A. Barclay, C.H.L. Kennard, J. Chem. Soc. (1961) 3289.
[11] S. Sen, M.K. Saha, T. Gupta, A.K. Karmakar, P. Kundu, S. Mitra, M.B. Hursthouse, K.M.A. Malik, J. Chem. Crystallogr. 28 (1998) 771.
[12] D.K. Towle, S.K. Hoffmann, W.E. Hatfield, P. Singh, P. Chaudhuri, Inorg. Chem. 27 (1988) 394.
[13] R.D. Mounts, T. Ogura, Q. Fernando, Inorg. Chem. 13 (1974) 802.
[14] E. Colacio, J.-P. Losters, R. Kivekäs, J.-P. Laurent, J. Ruiz, Inorg. Chem. 29 (1990) 4240.
[15] P.K. Loughlin, S.J. Lippard, J. Am. Chem. Soc. 106 (1984) 2328.
[16] J.N. van Niekerk, F.R.L. Schoening, Acta Cryst. 6 (1953) 227.
[17] R.B. Hull, Univ. Pittsburgh Bull. 35 (1938) 142.
[18] M.G. Brown, R. Chidambaram, Acta Cryst. B29 (1973) 2393.
[19] L. Rigamonti, S. Carlino, Y. Halibi, F. Demartin, C. Castellano, A. Ponti, R. Pievo, A. Pasini, Polyhedron 53 (2013) 157.
[20] U. Turpeinen, R. Hämäläinen, I. Mutikainen, Acta Cryst. C51 (1995) 2544.
[21] J. Medvecká, J. Halaška, K. Jomova, J. Moncol, Acta Chim. Slov. 5 (2012) 15.
[22] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, Science 283 (1999) 1148.
[23] A.S. Münch, F.O.R.L. Mertens, J. Mater. Chem. 22 (2012) 10228.
[24] M. Inoue, M. Kishita, M. Kubo, Inorg. Chem. 3 (1964) 239.
[25] C.S. Fountain, W.E. Hatfield, Inorg. Chem. 4 (1965) 1368.
[26] S. Ohba, M. Kato, T. Tokii, Y. Muto, O.W. Steward, Mol. Cryst. Liq. Cryst. 233 (1993) 335.
[27] C.D. Delfs, R. Bramley, Chem. Phys. Lett. 264 (1997) 333.
[28] J.R.J. Sorenson, J. Med. Chem. 19 (1976) 135.
[29] J.E. Weder, CT. Dillon, TW. Hambley, BJ. Kennedy, PA. Lay, JR. Biffin, HL. Regtop, NM. Davis, Coord. Chem. Rev. 232 (95) (2002).
[30] K. Jie, H. Xi-He, X. Jian-Hua, J. Zhu-Qing, H. Chang-Cang, Chin. J. Struct. Chem. 28 (2009) 15.
[31] M. Melník, M. Auderová, M. Holko, Inorg. Chim. Acta 67 (1982) 117.
[32] B. Kozlevčar, N. Lah, S. Makuc, P. Šegedin, F. Pohleven, Acta Chim. Slov. 47 (2000) 421.
[33] F. Hamza, G. Kickelbick, Macromolecules 42 (2009) 7762.
[34] T. Kawata, H. Uekusa, S. Ohba, T. Furukawa, T. Tokii, Y. Muto, M. Kato, Acta Cryst. B48 (1992) 253.
[35] R.E. del Sesto, A.M. Arif, J.S. Miller, Inorg. Chem. 39 (2000) 4894.
[36] A. Golobič, L. Ožbolt, F. Pohleven, I. Leban, P. Šegedin, Acta Chim. Slov. 53 (2006) 238.
[37] B. Kozlevčar, A. Murn, K. Podlipnik, N. Lah, I. Leban, P. Šegedin, Croat. Chem. Acta 77 (2004) 613.
[38] Bruker, SAINT, SADABS, AXS Inc., Madison, Wisconsin, USA, 2007.
[39] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
[40] A.L. Spek, Acta Cryst. D65 (2009) 148.
[41] L. Boniak, M.M. Borel, F. Busnot, A. Leclaire, Rev. Chim. Miner. 16 (1979) 501.
[42] S.M. Yu, C.-H. Park, P.-G. Kim, C. Kim, Y. Kim, Acta Cryst. E61 (2008) m881.
[43] R.E. Marsh, Acta Cryst. B55 (1999) 931.
[44] A.S. Münch, F. Katzsch, E. Weber, F. Mertens, J. Mol. Struct. 1043 (2013) 103.
[45] C. Fischer, F. Katzsch, E. Weber, Tetrahedron Lett. 54 (2013) 2874.
[46] F. Katzsch, E. Weber, Acta Cryst. E68 (2012) o2354.
[47] A. Münch, F. Katzsch, E. Weber, F.O.R.L. Mertens, Acta Cryst. E69 (2013) o908.
[49] M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, CrystEngComm 11 (2009) 1757.
[49] D. Eißmann, F. Katzsch, E. Weber, Struct. Chem. 23 (2012) 1131.
[50] T. Gruber, R. Nestler, W. Seichter, P. Bombicz, J. Mol. Struct. 1056 (2014) 319.