DINUCLEAR COPPER(II) ACETATE COMPLEX WITH CAFFEINE, A FAST MECHANOCHEMICAL SYNTHESIS

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A new dinuclear paddle-wheel copper(II) complex with caffeine was synthesized by the solvent-based and mechanochemical methods from copper(II) acetate and caffeine in a 1:1 molar ratio. Mechanochemical synthesis was found to be the fastest and easiest way to prepare the complex. The reaction proceeds with addition of small amounts of methanol or ethanol. The complex was characterized by FT-IR spectroscopy, elemental and thermoanalytical methods (TG and DSC) and X-ray diffraction methods. The molecular and crystal structure was determined by the single crystal X-ray diffraction method. The complex molecule consists of a centrosymmetric dinuclear unit, $[Cu_2(\mu\text{-Ac})_4(caf)_2]$, with two copper(II) atoms bridged by four acetato groups, and *N*-coordinated caffeine (caf) molecules in the apical positions.

Key words: copper(II); paddle-wheel structure; caffeine; crystal structure; mechanochemical synthesis

INTRODUCTION

Caffeine (3,7-dihydro-1,3,7-trimethyl-1*H*-purine-2,6-dione) is a purine alkaloid with very interesting pharmacological properties as a therapeutic agent with analeptic activity. The coordination chemistry of the purine type ligands has been subjected to intensive studies because of the importance of the interaction between these ligands and metal ions in many biological systems [1, 2].

A few crystal structures of copper(II) compounds with caffeine (caf) in which the copper(II) atoms are five coordinated have been described. Two monomeric examples are triaqua(caf)nitratocopper(II) nitrite [3] and aqua(caf)dichlorocopper(II) [4]. Caffeine usually prefers the nitrogen atom as the donor atom, especially in the copper(II) carboxylate complexes [5–14] (see Table 1). In $[Cu_2(flufenamato)_4(caf)(H_2O)]$ [15] two copper(II) atoms are bridged by four carboxylato groups, but one apical ligand is a caffeine molecule and the other one is a water molecule. The only example in the series of dimeric copper(II) carboxylates where both

apical position are occupied by *O*-coordinated caffeine molecules is $[Cu_2(3,5\text{-dinitrobenzoato})_4(caf)_2]$ [16]. The authors comment that the possible reason why this caffeine complex does not contain metal−N bonding is a steric effect caused by the size of the 3,5-dinitrobenzoato ligand.

In general, copper(II) carboxylates can contain a mononuclear, dinuclear or polynuclear structural unit. Scheme 1 shows some of the most frequently encountered coordination modes of carboxylate ligands in metal complexes.
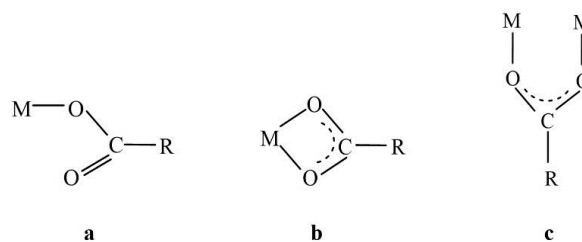
Scheme 1. Carboxylate coordination modes:
(a) monodentate; (b) chelate; (c) bidentate bridging

All of the dinuclear $[Cu_2(RCOO)_4XY]$ complexes, ($RCOO^-$ = carboxylate; X, Y = usually *N*- or *O*-donor ligands), have the paddle-wheel cage structure, as shown in Figure 1, in which each of the four carboxylate ligands is bound to both copper(II) ions in a bridging bidentate fashion. Each copper atom is coordinated by four oxygen atoms from the carboxylate ligands in the equatorial plane and can further accommodate a monodentate ligand, such as caffeine, in the apical position.

Some geometric parameters in the dinuclear complexes of the $[Cu_2(RCOO)_4(caf)_2]$ type, with caffeine as a *N*- or *O*-donor are presented in Table 1. In the Cambridge Structural Database (CSD) [17], Version 1.2.1 (2018), there are 12 such crystal structures. There is a relationship between the Cu···Cu distances and the distance of the copper(II) atom from the 4O equatorial basal plane towards the apical caffeine ligand, as the former is elongated the

latter also increases. However, there is no relationship with the Cu-N bond length. The observed differences in the geometry of the paddle-wheel unit can be attributed to the influence of different $RCOO^-$ ligands.
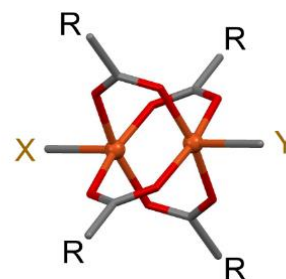

Figure 1. Drawing of a paddle-wheel unit.
$RCOO^-$ = carboxylate, X and Y are usually *N*- or *O*-donor ligands. Copper atoms are shown as spheres.

Table 1. Summary data of the $[Cu_2(RCOO)_4(caf)_2]$ complexes

Refcode* /Formula or name of $RCOO^-$	$d(Cu\cdots Cu)$ / Å	$d(Cu\text{-}O_{eq})$ (av)** / Å	$d(Cu\text{-}N_{ap})$ / Å	Cu-$4O_{eq}$ plane / Å	Ref.
KUBJUM $C_6H_5COO^-$	2.647(1)	1.967(2, 11)	2.222(3)	0.204	[5]
XIRCOQ (2*S*)-2-(6-methoxy-naphthalen-2-yl)propionato	2.649(1)	1.963(5, 16)	2.226(4)	0.216	[6]
QOPHOT $CH_3CH(Br)COO^-$ (monoclinic form)	2.6735(8)	1.943(4, 2)	2.183(5)	0.222	[7]
KIGMOD 2-[(2-Hydroxy-benzoyl)oxy]benzoato	2.680(1)	1.968(4, 15)	2.168(5)	0.219	[8]
REPVEO / $CH_3CH(Br)COO^-$ (triclinic form)	2.694(1)	1.966(5, 13)	2.231(7)	0.221	[9]
QOXLAQ 2-Iodobenzoato	2.7041(6)	1.966(2, 8)	2.238(2)	0.236	[10]
DAJVAL/ CH_2ClCOO^-	2.711(3)	1.98(4, 1)	2.23(4)	0.236	[11]
RERVAL $C_6H_5C(O)COO^-$	2.745(1)	1.975(4, 5)	2.161(5)	0.259	[12]
FOZKOM / CCl_3COO^- (benzene solvate)	2.852(2)	1.973(4, 17)	2.121(5)	0.315	[13]
KUHFUO / CCl_3COO^-	3.062(2)	2.011(2, 16)	2.0458(2)	0.415	[14]
			$d(Cu\text{-}O_{ap})$ / Å		
KELXEF 3,5-dinitrobenzoato	2.661(3)	1.958(2, 25)	2.180(3)	0.200	[16]
			$d(Cu\text{-}O_{ap})$ / Å $d(Cu\text{-}N_{ap})$ / Å		
KUHGUP*** / CCl_3COO^-	2.7364(9)	1.956(7, 12)	2.112(4) 2.115(4)	0.241	[14]

* in CSD
** the first number in parentheses is the e.s.d. and the second is the maximum deviation from the mean value
*** polymeric

Mechanochemical synthesis by neat grinding (NG) or liquid-assisted grinding (LAG), either done by using agate mortar and pestle or by ball-milling, is now a widely used method for synthesis without solvent or with just a small amount of a solvent. This is especially important in "green chemistry" by avoiding large amounts of organic solvents. In a review by Friščić and co-workers [18] syntheses by the NG or LAG methods resulting in different coordination polymers, metal-organic frameworks (MOFs) and metallodrugs have been discussed. They have shown that the reaction of copper(II) oxide with acetic acid by the LAG (water) method proceeded *via* an intermediate solvate of acetic acid with copper(II) acetate hydrate, which subsequently transformed into the final product copper(II) acetate hydrate [19]. Copper(II) acetate hydrate was also used in the first solvent-free synthesis of a porous MOF in a ball-milling reaction with isonicotinic acid. Technologically important porous framework HKUST-1, [$Cu_3(btc)_2$, btc = 1,3,5-benzenetricarboxylate], was obtained by grinding copper(II) acetate with 1,3,5-benzenetricarboxylic acid. In $Cu_3(btc)_2$ a pair of Cu^{2+} ions is chelated by four carboxylate bridges forming a paddle-wheel moiety. 1,3,5-benzenetricarboxylate is a linker molecule to three neighboring pairs of copper ions forming thus a 3D network [20, 21].

As a part of our interest in copper(II) complexes with molecules of biological importance [22, 23] we describe the synthesis and crystal structure of a new dinuclear copper complex tetrakis(μ-acetato-O:O')-bis(1,3,7-trimethylpurine-2,6-dione) dicopper(II), [$Cu_2(\mu$-Ac$)_4$(caf$)_2$], Ac = CH_3COO^-.

EXPERIMENTAL

General considerations

Chemicals were obtained from Sigma-Aldrich and used without previous purification. Elemental C, H, N analysis: Perkin-Elmer 2400 Series II CHNS analyzer in the Analytical Services Laboratories of the Ruđer Bošković Institute, Zagreb, Croatia. FT-IR spectra (KBr pellets): PerkinElmer Spectrum Two. TG and DTA curves were obtained by using Mettler-Toledo TGA/SDTA 851e module. The samples of about 2 to 5 mg were placed in alu-

minium pans (40 µl). The TGA and DTA curves were obtained with a heating rate of 10 °C min^{-1} under a oxygen flow of 200 ml min^{-1}. The samples were heated from room temperature up to 600 °C. DSC measurements were performed on a Mettler-Toledo DSC823^e module in aluminium pans (40 µl), heated in oxygen (200 ml min^{-1}) at a rate of 10 °C min^{-1}. The samples were heated from room temperature up to 500 °C. The data collection and analysis was performed using the program package STARe Software 9.01 [24]. A Retch MM200 grinder operating at 25 Hz frequency and teflon jars (14 ml in volume; using stainless steel grinding ball of 8 mm in diameter) were used for the grinding experiment.

Single-crystal X-ray diffraction

The single crystal X-ray diffraction data were collected at 293 K on an Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). The data were reduced using CrysAlisPRO software package [25]. The solution, refinement, and analysis of the structure was done using the software integrated in the WinGX system [26]. The structure was solved by the Patterson method using SHELXS [27] and refined by the full-matrix least-squares method based on F^2 against all data (SHELXL) [28]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced in calculated positions and refined using the appropriate riding model. Geometrical calculations were made using PLATON [29] and molecular graphics were prepared using Mercury [30], ORTEP-3 [31] and POV-Ray [32]. The main crystallographic data with refinement details are summarized in Table 2.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) data were collected on a PANalytical Aeris diffractometer in the Bragg-Brentano geometry using CuK$_\alpha$ radiation. The sample was contained on a zero background Si plate. Patterns were collected in the scan range of 2θ = 5–50° with the step size of 0.0027° and at 9 s per step. The data were visualized using the HighScore Plus program [33].

Table 2. Crystal data and details of crystal structure refinement

Compound	$[Cu_2(\mu\text{-}Ac)_4(caf)_2]$
Formula	$C_{24}H_{32}Cu_2N_8O_{12}$
M_r	751.66
Habit and colour	prism, dark blue-green
Crystal dimension / mm^3	$0.18 \times 0.21 \times 0.39$
Crystal system, space group	triclinic, P -1
a / Å	7.9252(2)
b / Å	9.1257(3)
c / Å	11.2138(3)
α / °	103.931(3)
β / °	100.629(2)
γ / °	99.372(3)
V / Å^3	755.17(4)
Z	1
D_c / g cm^{-3}	1.653
μ / mm^{-1}	1.483
F (000)	386
Θ range for data collection / °	$4.147 - 29.497$
h, k, l range	$-10{:}10; -12{:}12; -15{:}15$
No. of measured reflections	21467
No. independent reflections (R_{int})	4187
No. observed reflections, $I \geq 2\sigma(I)$	3889
R^a, wR^b [$I \geq 2\sigma(I)$]	0.0228
R, wR [all data]	0.0253
Goodness of fit on F^2, S^c	1.033
Max., min. electron density / e Å^{-3}	0.312, -0.208
Maximum Δ/σ	0.001
CCDC no.^{d}	1873412

[a] $R = \Sigma||F_o| - |F_c| / \Sigma|F_o|$

[b] $wR = [\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

[c] $S = \Sigma[w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$

[d] CCDC number contains the supplementary crystallographic data for this paper.
  These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Synthesis of $[Cu_2(\mu\text{-}Ac)_4(caf)_2]$

Mechanochemical synthesis: the liquid-assisted grinding method was used. Copper(II) acetate monohydrate (0.199 g, 1 mmol) and caffeine (0.194 g, 1 mmol) were weighed into a teflon jar, and 2 drops of methanol or ethanol were added. Milling was performed at room temperature for 1 hour.

Slurry method: neat grinding was performed by grinding copper(II) acetate (0.199 g, 1 mmol) and caffeine (0.194 g, 1 mmol) with a mortar and pestle for 15 min. A homogenized mixture of copper(II) acetate monohydrate and caffeine is obtained in this way (Fig. 2a, left). If two drops of methanol are ad-ded while grinding (LAG/MeOH) the powder is still only the mixture of reactants. The powder was then mixed with a few drops of methanol or ethanol in an Eppendorf tube to form a slurry. A change in color from cyan to dark blue-green occurs very fast. The reaction is completed in minutes (Figure 2a, right).

Solution–based synthesis: a solution of caffeine (0.194 g, 1 mmol) in 15 ml methanol (or ethanol) was added to a solution of copper(II) acetate monohydrate (0.199 g, 1 mmol) in 12 ml methanol. The mixture was heated to 60° and refluxed for 1 hour and then left to cool at room temperature.
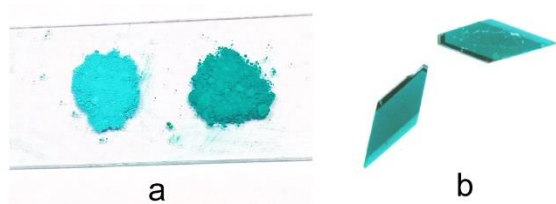
Figure 2. a) Powder on the left (light blue-green; cyan) was obtained after NG or LAG (mortar and pestle) for 15 min. It is a mixture of copper(II) acetate monohydrate and caffeine. Powder on the right is that of [Cu$_2$(μ-Ac)$_4$(caf)$_2$], obtained after addition of methanol or ethanol to the NG/LAG powder to form a slurry. It is of dark blue-green color.
b) Single crystals of [Cu$_2$(μ-Ac)$_4$(caf)$_2$] obtained by the solution–based synthesis.

Dark blue-green crystals were isolated by filtration, washed several times with cold ethanol and dried in air (Figure 2b). Anal. C$_{24}$H$_{32}$N$_8$O$_{12}$Cu$_2$ (751.66). Calc′d: C 38.34; H 4.26; N 14.91 %. Found: C 38.20; H 4.22; N 14.85 %.

RESULTS AND DISCUSSION

Synthesis

The complex was obtained by the reaction of copper(II) acetate monohydrate, Cu(Ac)$_2$·H$_2$O, and caffeine (C$_8$H$_{10}$N$_4$O$_2$) in a 1:1 molar ratio both by the solution–based method in methanol and mechanochemically by the LAG method with methanol or ethanol in a ball mill (Scheme 2). Taking into account the proper formula of the dimeric complex of copper(II) acetate monohydrate, [Cu$_2$(μ-Ac)$_4$(H$_2$O)$_2$], the ratio to caffeine is 1:2. It was found that the exchange of the two coordinated H$_2$O molecules with caffeine molecules occurs only by the assistance of methanol or ethanol.
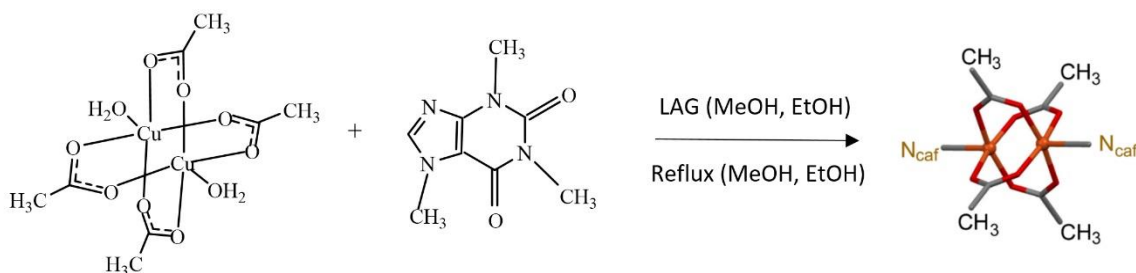
Scheme 2. Synthesis of [Cu$_2$(μ-Ac)$_4$(caf)$_2$]

Several other mechanochemical procedures were tried and the reaction products were monitored by PXRD. Neat grinding (NG) and LAG of copper(II) acetate monohydrate (Figure 3a) and caffeine (Figure 3b) in the 1:1 ratio with added water ground with a mortar and pestle were performed for 15 min. Such short grinding with or without addition of water resulted only in the mixture of copper(II) acetate and caffeine (Figure 3c). The same procedure was tried with LAG (methanol) but such short grinding with no compensation done for evaporation of methanol resulted in the same mixture. To obtain the complex with caffeine this mixture had to be soaked with methanol or ethanol to form a slurry (Figure 3g). PXRD pattern of the product of LAG for 1 hour in a ball mill with added water showed presence of copper(II) acetate monohydrate, however the highest caffeine peak almost disappeared and two new low angle peaks formed that could not be assigned, but there were no peaks of the caffeine complex (Figure 3d). On contrary, LAG with methanol or ethanol in a ball mill for 1 hour resulted in the caffeine complex [Cu$_2$(μ-Ac)$_4$(caf)$_2$] (Figure 3h). The same complex was obtained by the solution-based method which gave single-crystals suitable for the crystal structure determination (Figure 3i).

Tella *et al*. [34] have recently published a synthesis of [Cu(caf)$_2$(H$_2$O)(Ac)]Ac by both mechanochemical and solution–based methods, however the molar ratio of Cu(Ac)$_2$·H$_2$O and caffeine was 1:2 ([Cu$_2$(μ-Ac)$_4$(H$_2$O)$_2$]:caffeine = 1:4). Therefore, during this synthesis the dinuclear paddle-wheel unit would be broken and a mononuclear complex obtained. The authors have characterized this complex by elemental analysis, FT-IR, UV–Vis and 1H NMR spectra but not by the single-crystal X-ray diffraction. The proposed structure consists of copper atom coordinated with two bidentately donating caffeine ligands through the nitrogen atom of the imidazole group and the oxygen atom of the pyrimidine group, a water molecule and an acetate ligand. One acetate is proposed to be a free anion. A caf-

feine molecule to be bidentately coordinating one copper atom we consider highly unlikely. In our opinion only a polymeric structure would be possible. We followed their synthetic procedure (1 mmol of copper(II) acetate and 2 mmol of caffeine were ground together with a mortar and pestle for 15 min; a bluish-green powder was washed with methanol) and collected the PXRD pattern of the product before washing with methanol and obtained only a mixture of copper(II) acetate monohydrate and caffeine, with more caffeine than in our 1:1 synthesis (Figure 3e). Upon washing with a small amount of

methanol the same caffeine complex is formed as in our synthesis but there is an excess of unreacted caffeine (Figure 3f). There are no peaks that correspond to their powder pattern. It has to be noted that they have made an error and instead of a powder pattern of copper(II) acetate monohydrate they gave a pattern of copper(II) chloride dihydrate.

Contrary to Tella *et al.*, the same complex as ours was obtained by a solution-based method in ethanol (reflux for 4 hours) by Hamdani *et al.* [35]. The ratio of copper(II) acetate monohydrate and caffeine was 1:2, and not 1:1 as in our synthesis.
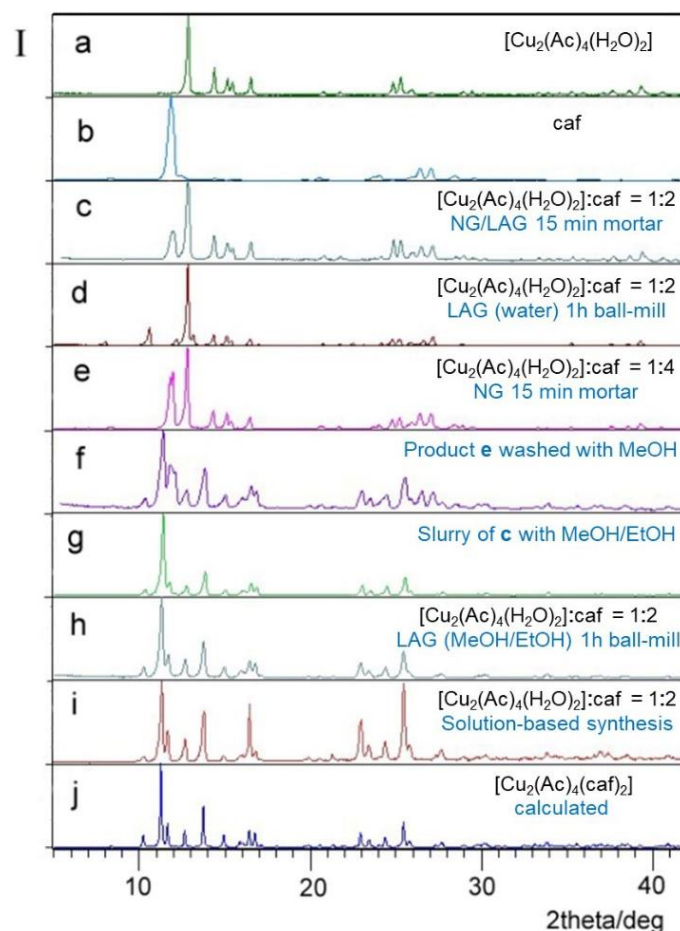

Figure 3. Powder diffractograms of: (a) copper(II) acetate monohydrate (Cu(Ac)$_2$·H$_2$O = [Cu$_2$(μ-Ac)$_4$(H$_2$O)$_2$]); (b) caffeine; (c) product of NG or LAG (water) for 15 min by hand; (d) product of LAG (water) for 1 hour in a ball-mill; (e) product of NG for 15 min by hand (procedure by Tella *et al.*); (f) product (e) washed with MeOH; (g) product (c) with added MeOH or EtOH to form a slurry; (h) product of LAG (MeOH or EtOH) for 1 hour in a ball mill; (i) solution-based synthesis; (j) calculated powder pattern from the crystal structure of [Cu$_2$(μ-Ac)$_4$(caf)$_2$].

FT-IR spectroscopy

Table 3 presents the most important IR spectral bands for caffeine, copper(II) acetate monohydrate and [Cu$_2$(μ-Ac)$_4$(caf)$_2$] obtained *via* the solution–based and mechanochemical methods. The

carboxylate stretching frequencies $\nu(-COO^-)_{asym}$ at 1620 cm^{-1} and $\nu(-COO^-)_{sym}$ at 1426 cm^{-1} are characteristic for copper(II) carboxylate compounds [15, 36, 37] (Figure 4). The two strong band at 1700 cm^{-1} and 1660 cm^{-1} were attributed to $\nu(CO)_{asym}$ and $\nu(CO)_{sym}$ / $\nu(-C=N)$ in free caffeine, the latter

shifted to 1650 cm^{-1} in the copper complex. The δ(HCN) + ν_{ring}(imid) + ν_{ring}(pyrim) stretching and deformation of the heterocyclic imidazol and pyrimidine fragments was found at 1550 cm^{-1} [38, 39]. This band shifted to 1541 cm^{-1} in the complex indicating that the (C=N) imidazole fragment of caffeine is involved in coordination with the metal ion through the N9 nitrogen atom. Hamdani *et al*. obtained the same IR spectrum as ours indicating that they also prepared [Cu$_2$(μ-Ac)$_4$(caf)$_2$].

Table 3. Characteristic IR bands (cm^{-1}) in caffeine, copper(II) acetate monohydrate and [Cu$_2$(μ-Ac)$_4$(caf)$_2$]

Caffeine	Copper(II)acetate monohydrate	[Cu$_2$(μ-Ac)$_4$(caf)$_2$]	Attribution
1700		1700	ν(−C=O)$_{asym}$
1660		1650	ν(−C=O)$_{sym}$/ν(−C=N)
1550		1541	δ(HCN) + ν_{ring}(imid) + ν_{ring}(pyrim)
	1610	1620	ν(−COO$^-$)$_{asym}$
	1590		
	1435	1426	ν(−COO$^-$)$_{sym}$
	1415		

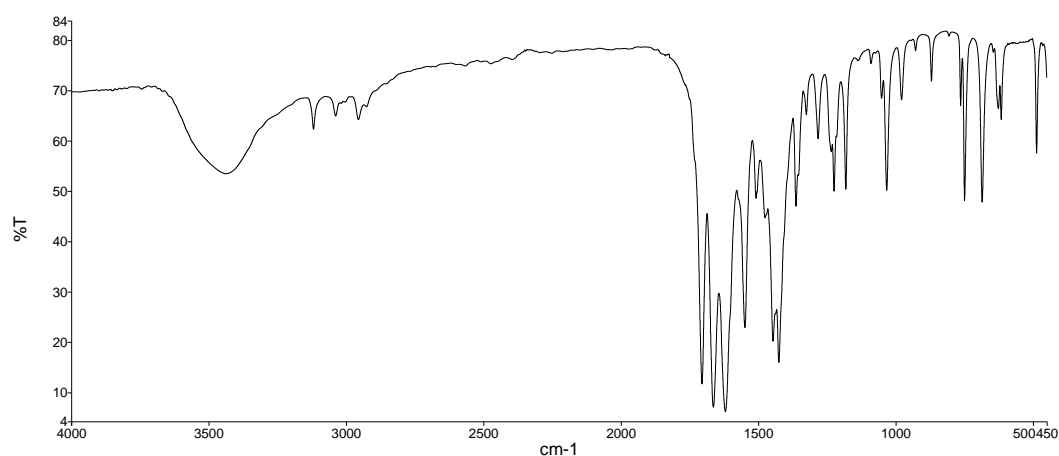**Figure 4.** Infrared spectra of [Cu$_2$(μ-Ac)$_4$(caf)$_2$] obtained *via* the solution–based or mechanochemical method (LAG, MeOH)

Thermal analysis

Complex [Cu$_2$(μ-Ac)$_4$(caf)$_2$] was heated from room temperature to 600 °C (TG) and from room temperature to 500 °C (DSC) in an oxygen atmosphere. The TG curve of the complex shows two degradation steps. The first step between 234 and 272 °C is accompanied by a 32.3 % weight loss (calculated 31.4 %) corresponding to the elimination of the acetato ligands. This step is represented by two exothermic peaks at 255 and 287 °C on the DSC curve. Three exothermic peaks with maxima at 363, 368 and 375 °C are associated with the elimination of two caffeine molecules (observed weight loss 45.1 %, calculated 51.6 %). The remaining residue of 21.5 % at 600 °C is CuO.

X-ray crystal structure

The X-ray structure of [Cu$_2$(μ-Ac)$_4$(caf)$_2$] is depicted in Figure 5. The complex molecule contains the dinuclear paddle-wheel unit with two copper atoms and four bridging acetate ligands. It is centrosymmetric with the center of inversion located between the two copper atoms so there is a half of the molecule in the asymmetric unit. Each of the copper(II) atoms is coordinated by four acetato groups as equatorial ligands and one nitrogen atom from the caffeine ligand, localised at the apex of a distorted square pyramid.
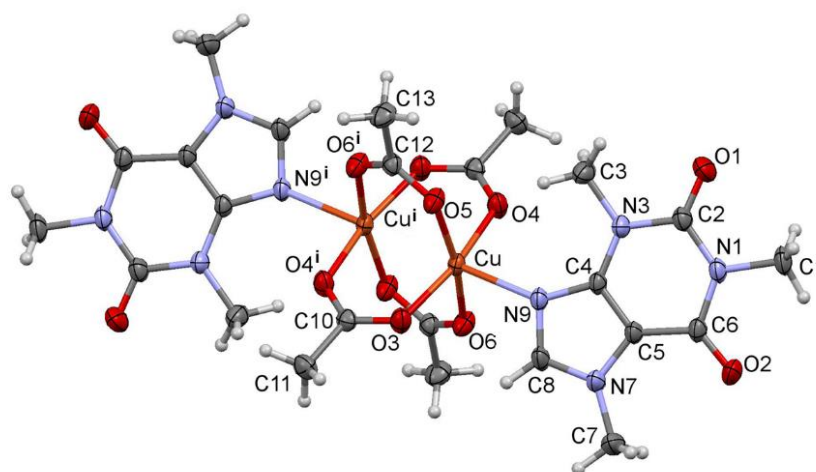
Fig. 5. Molecular structure of $[Cu_2(\mu\text{-}Ac)_4(caf)_2]$ with the atom labeling scheme. Symmetry code: *i* = 1-*x*, 1-*y*, -*z*. The ellipsoids are at the 40 % probability level. Hydrogen atoms are depicted as spheres of arbitrary radii.

The Cu···Cu distance of 2.6350(3) Å is the shortest one among the known dinuclear $[Cu_2(RCOO)_4(caf)_2]$ complexes (Table 1). The displacement of the Cu atom from the equatorial plane (atoms O3−O6) toward the apical atom of N(9) amounts to 0.202(1) Å. The apical Cu−N(caf) bond length is 2.2585(10) Å being the longest one in comparison to other complexes (Table 1). Each Cu(II) ion has four oxygen atoms from different carboxylate groups in the equatorial positions, with Cu−O distances in the range from 1.9689(10) to 1.9716(10) Å, Table 4. These values are comparable to those found in other Cu(II) carboxylates.

The geometry of the caffeine ligand linked to the metal center indicates delocalization of π- electrons within the pyrimidine and imidazole ring of caffeine. Both rings are planar with a maximum deviation of N9 amounting to 0.025(1) Å from the least-squares plane through the ring atoms. Maximum ring substituent deviation from this plane is that of C(3) being 0.066(2) Å.

The complex structure is stabilized by weak C3-H···O5 intramolecular hydrogen bond. There are also only weak intermolecular hydrogen bonds of the C-H···O type interconnecting the complex molecules in a 3D structure since C-H groups are the only available hydrogen bond donors. The relevant characteristics of H-bonds are given in Table 5 and the packing is shown in Figure 6.

Table 4. Selected bond distances (Å) and valence angles (°) for $[Cu_2(\mu\text{-}Ac)_4(caf)_2]$

Bond distances	
Cu−O3	1.9716(10)
Cu−O4	1.9554(10)
Cu−O5	1.9624(10)
Cu−O6	1.9689(10)
Cu−N9	2.2585(10)
Bond angles	
O3−Cu−O4	168.02(4)
O3−Cu−O5	90.96(5)
O3−Cu−O6	87.43(5)
O5−Cu−O6	168.31(4)
O3−Cu−N9	95.24(4)
O4−Cu−N9	96.51(4)
O5−Cu−N9	99.38(4)
O6−Cu−N9	92.30(4)

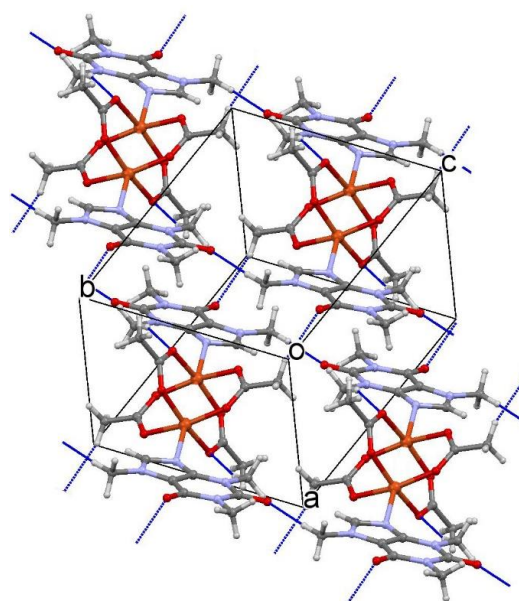**Figure 6.** Packing diagram of $[Cu_2(\mu\text{-}Ac)_4(caf)_2]$ in the unit cell. Hydrogen bonds are shown by blue dotted lines.

Table 5. Hydrogen bonding parameters

D−H⋯A	Distance /Å			Angle /°	Symmetry code
	D−H	H⋯A	D⋯A	D−H⋯A	
C3−H⋯O5	0.96	2.49	3.4028(19)	159	
C7−H⋯O1	0.96	2.28	3.232(2)	172	$x, -1+y, z$
C11−H⋯O2	0.96	2.53	3.451(2)	161	$1-x, 1-y, 1-z$

CONCLUSION

By direct reaction of copper(II) acetate monohydrate with caffeine in the 1:1 molar ratio, either by the solution-based method or mechanochemically (LAG with methanol or ethanol) the dinuclear complex, $[Cu_2(\mu\text{-}Ac)_4(caf)_2]$, was prepared. It was found that the addition of methanol or ethanol is necessary for the formation of the complex since NG or LAG with water did not result in the complex formation. We have found that the replacement of water molecules by caffeine molecules in the paddle-wheel copper(II) acetate complex proceeds also in a slurry at room temperature only by the addition of a few drops of methanol or ethanol to the homogenized mixture of the reactants (with a mortar and pestle for 15 min). This is the fastest and easiest way to prepare the complex. The obtained complex consists of the paddle-wheel dimeric $Cu_2(O_2CCH_3)_4$ unit with N-coordinated caffeine molecules in both apical positions. Each copper(II) atom is five coordinated (distorted square-pyramidal) with four oxygen atoms from four acetato anions in the equatorial positions and the caffeine N atom in the apical position (Cu-N 2.2585(10) Å). The Cu⋯Cu distance is 2.6350(3) Å. The copper(II) atoms are displaced from the O4 equatorial plane by 0.202(1) Å toward the apical N-atom of caffeine.

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БИНУКЛЕАРЕН БАКАРЕН(II) АЦЕТАТЕН КОМПЛЕКС СО КОФЕИН, БРЗА МЕХАНОХЕМИСКА СИНТЕЗА

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Синтетизиран е нов бинуклеарен пропелерски тип (paddle-wheel) на бакарен(II) комплекс со кофеин со помош на механохемиски метод заснован на растворувач, а поаѓајќи од бакар(II) ацетат и кофеин во моларен сооднос 1:1. Најдено е дека механохемиската синтеза е најбрз и најлесен начин за подготовка на комплексот. Реакцијата се одвива со додавање на мало количество метанол или етанол. Комплексот е карактеризиран со помош на FT-IR спектроскопија, анализа на хемиските елементи, термоаналитички методи (TG and DSC) и метод на рендгенска дифракција. Молекулската и кристалнта структура се определени со помош на рендгенска дифракција од монокристал. Комплексната молекула се состои од центросиметрична бинуклеарна единка од типот [$Cu_2(\mu\text{-}Ac)_4(caf)_2$], што ја чинат два бакарни(II) атома премостени преку четири ацетатни групи, како и *N*-координирани кофеински (caf) молекули во апикални положби.

Клучни зборови: бакар(II); пропелерска (paddle-wheel) структура; кофеин; кристална структура; механохемиска синтеза