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[Cu(μ-MeCO$_2$)$_2$(4-Bzpy)]$_2$ (4-Bzpy = 4-benzylpyridine): Study of the intermolecular C–H···O hydrogen bonds at two temperatures

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[Cu(μ-MeCO$_2$)$_2$(4-Bzpy)]$_2$ (4-Bzpy = 4-benzylpyridine) has been synthesized by reaction of [Cu(μ-MeCO$_2$)$_2$(H$_2$O)]$_2$ with 4-Bzpy in methanol at room temperature. The compound was characterized by Elemental Analysis, ATR-FTIR and X-ray Powder Diffraction. The molecular structure was determined by single crystal X-ray diffraction analysis at 100 K and 303 K. The compound consists of binuclear units where both Cu(II) atoms are linked by four *syn-syn* carboxylate bridges, showing a paddle-wheel unit. The role of C–H···O hydrogen bonds in the establishment of its supramolecular network is discussed, comparing the resulting structural parameters at the two different temperatures. Finally, the thermal variation of X_pT for compound **1** has also been studied, suggesting an antiferromagnetic Cu···Cu interaction ($J = -311\ \mathrm{cm}^{-1}$), which agrees with the presence of four μ-κO-κO′ carboxylates bridging the metallic centers in the binuclear complex.

1. Introduction

The synthesis, crystal structure and properties of numerous copper(II) carboxylates have already been extensively studied, garnering great interest due to their diverse structural features [1–4], spectroscopic, magnetic and catalytic activities [5,6]. Furthermore, a large number of paddle-wheel type binuclear copper(II) carboxylate adducts [Cu(μ-RCO$_2$)$_2$(L)]$_2$, where L is an apical ligand with oxygen or nitrogen atom, have been reported in the literature, many of them featuring pyridine groups [7–12]. In their synthesis, metal carboxylates, along with *N*- and *O*- donor atoms, have often been used with the aim of constructing paddle-wheels with mixed ligands, which might have interesting structural features with useful applications.

Binuclear paddle-wheel Cu(II) units have attracted attention as building-blocks for Supramolecular Metal Organic Frameworks (SMOFs), porous materials sustained by intermolecular weak forces [13,14]. SMOFs have attracted great attention due the possibility of out-performing Metal Organic Frameworks (MOFs) in its industrial applications due to enhanced host-guest interactions and wet-processability. Among the weak forces that hold SMOFs together, hydrogen bonds have a special importance as they are among the strongest intermolecular forces, and play a central role in crystal engineering [15,16]. Beyond the classical X–H···O bond (X = *N*, *O* or halogen), nowadays the importance of C–H···O bonds is widely recognized, despite strong controversy over past years [17–20]. Although C–H···O bonds have been extensively studied regarding organic compounds, its importance in coordination chemistry is now being recognized [21–23].

As a continuing effort to enhance the comprehension of structure, reactivity and different properties of the copper(II) carboxylate compounds, we employed pyridine ligands with the potential to incorporate intra- and intermolecular interactions (e.g. hydrogen bond, π-π stacking, etc) [1,2]. In this context, we have studied the synthesis and structural characterization of 1,3-benzodioxole-5-carboxylic acid (HPip) and different amines (3-phenylpyridine and 4-phenylpyridine) with Zn(MeCO$_2$)$_2$·2H$_2$O and Cd(MeCO$_2$)$_2$·2H$_2$O obtaining the compounds [Zn(μ-Pip)$_2$(3-Phpy)]$_2$, [Zn(μ-Pip)$_2$(4-Phpy)]$_2$, [Cd(μ-Pip)(Pip)(3-Phpy)$_2$]$_2$ and [Cd(μ-Pip)(Pip)(4-Phpy)$_2$]$_2$ coordination dimers [24]. We also studied the

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reaction of the same ligand (HPip) with $[Cu(\mu\text{-}MeCO_2)_2(H_2O)]_2$ and pyridine ligands (dPy = 3-Phpy, 4-Bzpy and 4-Phpy) obtaining $[Cu(Pip)_2(3\text{-}Phpy)(H_2O)]$ and $[Cu(Pip)_2(4\text{-}Bzpy)_2][Cu(Pip)_2(4\text{-}Bzpy)_2(HPip)]$ monomeric compounds and $[Cu(\mu\text{-}Pip)_2(dPy)]_2$ (dPy = 3-Phpy, 4-Bzpy) and $[Cu(\mu\text{-}Pip)(Pip)(4\text{-}Phpy)_2]_2$ dimeric compounds [25]. Moreover, when the reaction of HPip and $[Cu(\mu\text{-}MeCO_2)_2(H_2O)]_2$ in 1:1 M:L is assayed, heteroleptic compound is obtained $[Cu(\mu\text{-}Pip)(\mu\text{-}MeCO_2)(MeOH)]_2$ [26].

Recently in our group, we have assayed the reaction of $[Cu(\mu\text{-}MeCO_2)_2(H_2O)]_2$ and pyridine ligands (dPy = 3-Phpy, 2-Bzpy and 4-Acpy) obtaining always paddle-wheel compounds $[Cu(\mu\text{-}MeCO_2)_2(dPy)]_2$ [27]. As a continuation of this work, in this manuscript we are interested in the reaction of $[Cu(\mu\text{-}MeCO_2)_2(H_2O)]_2$ with 4-Bzpy. In particular, we report the synthesis, IR spectroscopy and X-ray crystal structure of the resulting compound $[Cu(MeCO_2)_2(4\text{-}Bzpy)]_2$ (**1**). Furthermore, the X-ray crystal structure was determined at two different temperatures, 100 K (**1A**) and 303 K (**1B**), which allow to study the effect of temperature in its supramolecular structure, with special focus on the role of C–H···O hydrogen bonds. Finally, magnetic studies for this compound were also carried out.

2. Results and discussion

2.1. Synthesis and general characterization

Complex **1**, was prepared in MeOH at room temperature *via* combination of $[Cu(\mu\text{-}MeCO_2)_2(H_2O)]_2$ and 4-benzylpyridine (4-Bzpy), yielding complex $[Cu(\mu\text{-}MeCO_2)_2(4\text{-}Bzpy)]_2$, a paddle-wheel product. In this reaction, the coordinated apical H_2O molecules were displaced by the pyridine-derived ligand. The corresponding crystals suitable for X-ray crystallographic analysis were grown *via* slow evaporation of their mother liquors. The obtained compound is green and elemental analyses agree with the proposed formula. Phase purity of the compound was confirmed *via* a whole pattern matching process. The experimental powder X-ray diffraction (PXRD) is compared against a pattern calculated using DAjust software [28], which considers the defining parameters (space group, symmetry group, unit cell parameters ....) of the solved crystal structure. The result is graphically represented using WinPlotR software [29] (SI, Fig. S1).

Shifts in the ATR-FTIR spectrum of the compound compared to the reagents, $[Cu(\mu\text{-}MeCO_2)_2(H_2O)]_2$ and 4-Bzpy (SI, Fig. S2-S4), confirms their coordination to the metal centre. Bands assignable to carboxylate group give key information about the coordination mode. This compound displays the bands attributable to carboxylate anion at 1600 cm^{-1} for $\nu_{as}(COO)$ and 1423 cm^{-1} for $\nu_s(COO)$, the difference between $\nu_{as}(COO)$ and $\nu_s(COO)$ is 177 cm^{-1}, indicating bidentate bridging coordination mode of the acetate group [30,31]. The bands attributable to the aromatic groups $\nu(C{=}C)_{ar}$, $\nu(C{=}N)_{ar}$, $\delta(C{-}H)_{ip}$ and $\delta(C{-}H)_{oop}$ are also observed [32]. The IR spectral data thus clearly lend support to the structure determined by the X-ray diffraction method (SI, Fig. S4).

2.2. Crystal structure of $[Cu(\mu\text{-}MeCO_2)_2(4\text{-}Bzpy)]_2$ (1)

The compound was isolated as green prism-like crystals. Single crystal X-ray diffraction revealed that the compound is $[Cu(\mu\text{-}MeCO_2)_2(4\text{-}Bzpy)]_2$ (**1**) and crystallizes in the monoclinic space group $P2_1/c$. The representation is shown in Fig. 1. Selected bond distances and angles are provided in Table 1.

The Cu atoms adopt the $[CuO_4N]$ coordination mode, with four oxygen atoms from different carboxylates and one nitrogen atom from 4-Bzpy ligand. The structure consists in a centrosymmetric binuclear copper(II) unit and is typical of binuclear $[M_2(carboxylate)_4L_2]$ complexes [33]. The carboxylate groups of the acetate ligands display a paddle-wheel-like arrangement, with four bridging acetate ligands in a *syn-syn* coordination mode. At 100 K, the Cu····Cu separation is 2.6222 (6) Å, whereas at 303 K is 2.6311 (10). Both values are comparable to those reported for paddle-wheel complexes with similar structure [25,26,34,35]. The tetra-

Table 1
Selected bond lengths (Å) and bond angles (°) for **1A** (100 K) and **1B** (303 K).

Bond length (Å)	1A (100 K)	Bond length (Å)	1B (303 K)
Cu(1)–O (1)#1	1.9637 (18)	Cu(1)–O (1)	1.975 (4)
Cu(1)–O (2)	1.9690 (18)	Cu(1)–O (2)#1	1.963 (4)
Cu(1)–O (3)	1.9695 (18)	Cu(1)–O (3)	1.962 (4)
Cu(1)–O (4)#1	1.9715 (18)	Cu(1)–O (4)#1	1.973 (4)
Cu(1)–N (1)	2.1828 (19)	Cu(1)–N (1)	2.191 (4)
Cu(1)–Cu(1)#1	2.6222 (6)	Cu(1)–Cu(1)#1	2.6311 (10)
Bond Angles (°)			
O (1)#1-Cu(1)-O (2)	168.60 (7)	O (1)-Cu(1)-O (2)#1	167.81 (15)
O (1)#1-Cu(1)-O (3)	90.27 (9)	O (1)-Cu(1)-O (3)	88.52 (18)
O (2)-Cu(1)-O (3)	88.58 (8)	O (2)#1-Cu(1)-O (3)	89.67 (17)
O (1)#1-Cu(1)-O (4)#1	89.30 (8)	O (4)#1-Cu(1)-O (1)	90.26 (18)
O (2)-Cu(1)-O (4)#1	89.58 (8)	O (2)#1-Cu(1)-O (4)#1	89.04 (18)
O (3)-Cu(1)-O (4)#1	168.52 (7)	O (3)-Cu(1)-O (4)#1	168.12 (15)
O (1)#1-Cu(1)-N (1)	93.52 (7)	O (1)#1-Cu(1)-N (1)	94.62 (15)
O (2)-Cu(1)-N (1)	97.88 (7)	O (2)#1-Cu(1)-N (1)	97.57 (15)
O (3)-Cu(1)-N (1)	94.54 (7)	O (3)-Cu(1)-N (1)	98.11 (15)
O (4)#1-Cu(1)-N (1)	96.94 (7)	O (4)#1-Cu(1)-N (1)	93.77 (15)

#1 -x+1,-y+1,-z+1.

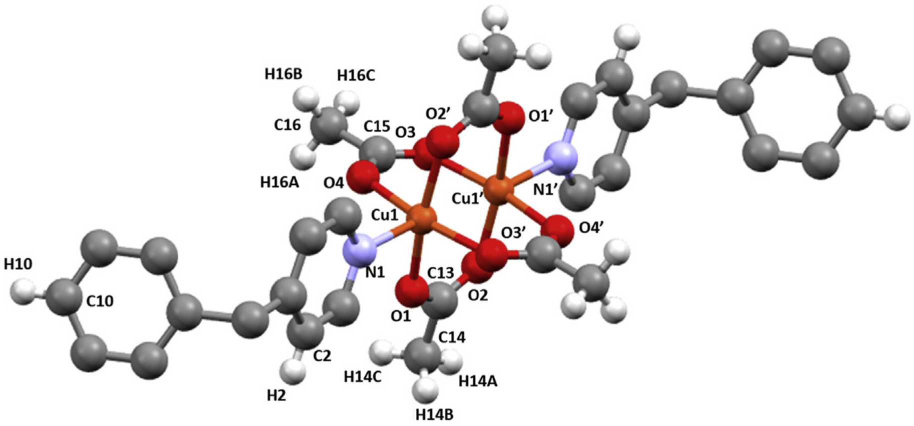

Fig. 1. $[Cu(\mu\text{-}MeCO_2)_2\ (4\text{-}Bzpy)]_2$ at 100 K (**1A**) showing the labelling scheme for relevant atoms. See Table 1 for selected values of bond lengths and bond angles.