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Novel Acetate Binding Modes in $[Na_2Cu(CH_3COO)_4(H_2O)]\cdot H_2O$

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A new copper(II) acetate, $[Na_2Cu(CH_3COO)_4(H_2O)]\cdot H_2O$ (**1**), has been crystallized from an aqueous solution containing sodium acetate and copper(II) acetate monohydrate in a 4:1 ratio and the structure determined by X-ray crystallography. **1** crystallizes in the monoclinic space group *P*2(1)/*c*, with $a = 16.638(3)$ Å, $b = 11.781(2)$ Å, $c = 15.668(3)$ Å, $\beta = 90.11(3)°$, $V = 3071.0(11)$ Å^3, and $Z = 4$. In the asymmetric unit, sodium ions bridge two crystallographically unique square planar $[Cu(CH_3COO)_4]^{2-}$ units to their symmetry-generated neighbors to form corrugated 2D sheets of $Na_2Cu(CH_3COO)_4$, which are held together by H-bonding interactions involving the waters of crystallization. In contrast, the structures of known sodium copper acetates are better described as 3D frameworks. The metal centers are bridged by a number of acetates in novel coordination modes. The square planar Cu(II) geometry generated by oxygen atoms from four different acetates is an unexpected feature given the weak ligand field provided by the acetate ligands.

Introduction

The properties and supramolecular behavior of copper(II)/carboxylates have been studied extensively since the structure of $Cu_2(CH_3COO)_4\cdot 2H_2O$ was first reported five decades ago.[1] Although much of the attention has focused on analogues of this complex, various Cu(II) carboxylate derivatives that incorporate alkali metal ions, often sodium, have been reported in the last 20 years for ligands such as croconate,[2] picolinate,[3] azamacrocycle acetate derivatives,[4,5] amino acids,[6,7] crown ethers[8] and alkoxo anions.[9] These studies have sparked interest in understanding the influence of alkali metal ions on the structure and properties of transition metal complexes. Recent attempts to synthesize double salts consisting of alkali metal cations and Cu(II) acetate anions met with limited success in the case of sodium.[10] Although the structures of two compounds of composition $NaH[Cu_2(CH_3COO)_6]$ have been reported,[11,12] both of these structures contain the well-characterized $[Cu_2(CH_3COO)_4]$ binuclear units,[1] linked by acetate-bridged Na^+ ions to generate a 3D network. The Na^+ salt of the Cu(II) propionate, $Na[Cu_4(C_2H_5COO)_9(H_2O)]$, also forms a 3D framework in which the Cu(II) propionate complexes are linked by Na^+ ions.[13] Recently, Ng et al.[7] reported the formation of a 1:1 sodium perchorate−$[Cu(betaine)_4]^{2+}$ adduct, $[Cu\{(CH_3)_3NCH_2CO_2\}_4(NaClO_4)](ClO_4)_2$, in which the Cu(II) center is, perhaps unexpectedly, square planar. We report the synthesis and X-ray structure of $[Na_2Cu(CH_3COO)_4(H_2O)]\cdot H_2O$ (**1**). This complex forms a 2D layered structure which features a number of novel acetate binding modes and, to our knowledge, incorporates the first example of square-planar $[Cu(CH_3COO)_4]^{2-}$ anions binding to Na^+.

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Experimental Section

Reagents and Physical Techniques. Commercial reagents were used as supplied without further purification. IR spectra were recorded on a Perkin-Elmer 1600 series instrument as KBr disks. Electronic spectra were recorded on a Cary 5G UV−visible-NIR spectrophotometer. The magnetic moment was measured using a Faraday balance incorporating a 4 in. Newport electromagnet.

Preparation of $[Na_2Cu(CH_3COO)_4(H_2O)]\cdot H_2O$ (1). The following procedure was devised following the discovery of crystals of **1** in a solution containing 1-benzyl-4-acetato-1,4,7-triazacyclononane trihydrochloride, 2 equiv of copper(II) chloride, sodium hydroxide, and excess sodium acetate. A solution of sodium acetate (3.0 g, 36 mmol) in distilled water (10 mL) was stirred and heated to between 80 and 90 °C in a beaker on a hotplate. Copper(II) acetate monohydrate (1.80 g, 9.0 mmol) was then added in small portions over a 10 min period with continued stirring and heating, the solid being allowed to completely dissolve before further additions, to give a deep blue clear solution from which a light blue powder started to precipitate. After 30 min the solution was cooled to room temperature and left open to the atmosphere in an evaporating dish. The light blue powder continued to precipitate for several hours. After a few days, small, isolated clusters of deep blue crystals of **1** formed. The crystals were separated from the light blue powder by several washings with ethanol (95%) in a test tube with stirring. This suspended most of the powder in the liquid, which could be decanted leaving the crystals of **1** at the bottom of the tube. When exposed to air for several minutes the crystals appear to lose solvent and develop a fine white film on the surface. Yield: 1.13 g (32%). Anal. Calcd for **1**: C, 25.2; H, 4.2. Found: C, 25.4; H, 4.1. IR (KBr) ν/cm^{-1}: 3474 (s, OH), 3004, 2931 (w, CH), 1617, 1583, 1561, 1406 (s, −COO), 1344 (m), 1050 (w), 1016 (w), 938 (w), 677 (w), 622 (w). UV/visible spectrum (diffuse reflectance, nm): 280, 350−400 (br), 580−670 (br). Magnetic moment: $\mu_{\text{eff}} = 1.88\ \mu_B$ at 293 K. Anal. of light blue powder. Found: Calcd for $\{[0.85Cu(OH)(CH_3COO)\cdot H_2O][0.15Cu(OH)_2]\}$: C, 13.7; H, 3.6; C, 13.8; H, 2.6; Na, 0; Cu, 42.5. Na, 0; Cu, 42.8. IR (KBr) ν/cm^{-1}: 3482, 3199 (s, OH), 3000 (w, CH), 1572, 1524, 1431, (vs, −COO), 1341 (w), 1141 (w), 1028 (w), 980 (w), 909 (m), 680 (m), 650 (w), 619 (w).

X-ray Crystallography. A portion of a crystal of **1** was cut under a microscope and mounted on a glass fiber. Diffraction data for **1** was collected on an Enraf-Nonius CCD diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 123(2) K using ϕ and/or ω scans. Data were corrected for Lorentz and polarization effects, and absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Water hydrogen atoms were located on Fourier difference maps and refined isotropically without restraint with the exception of one on O(18). The difficulty in locating the second hydrogen on O(18) may be due to the presence of only one suitable H-bond acceptor in the vicinity of this water molecule, in contrast to O(20), which has both of its hydrogen atoms participating in interactions with an acetate oxygen (O(11)) and O(18). The structure was solved by direct methods, and refinement on F^2 used the full matrix least-squares methods of SHELXS-97[14] and SHELXL-97,[15] respectively. The program X-Seed[16] was used as an interface to the SHELX programs, and to prepare the figures. Crystal data is given in Table 1, and selected bond lengths and intermetallic distances and angles are given in Table 2. Thermal ellipsoids are drawn at 30% probability.

Table 1. Crystal Structure and Refinement Data for **1**

empirical formula	$C_{16}H_{32}Cu_2Na_4O_{20}$
fw, g mol^{-1}	763.46
λ, Å	0.71073
crystal system	monoclinic
space group	$P2(1)/c$
a, Å	16.638(3)
b, Å	11.781(2)
c, Å	15.668(3)
β, deg	90.11(3)
V, Å^3	3071.0(11)
Z	4
ρ_{calcd}, g/cm^3	1.649
μ(Mo Kα), mm^{-1}	1.521
θ range, deg	3.00−28.28
no. of measd reflns	28880
no. of obsd reflns [$I > 2\sigma(I)$]	7176
GOF on F^2	1.182
R_1[a]	0.0735
wR_2[b]	0.1385
largest diff peak and hole, e Å^{-3}	+0.450, −0.942

[a] $\sum||F_o| - |F_c||/\sum|F_o|$. [b] $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths and Intermetallic Distances (Å) and Angles (deg) for Construct **A** in **1**

Cu(1)−O(19)	1.933(4)	Na(2)−O(6)#5[a]	2.432(4)
Cu(1)−O(9)	1.962(4)	Na(2)−O(4)	2.771(5)
Cu(1)−O(6)	1.967(4)	Na(4)−O(9)	2.323(4)
Cu(1)−O(12)	1.978(4)	Na(4)−O(4)#6	2.336(4)
Na(2)−O(10)#5	2.342(5)	Na(4)−O(16)#8	2.380(5)
Na(2)−O(19)	2.352(4)	Na(4)−O(22)#8	2.397(5)
Na(2)−O(16)#5	2.369(4)	Na(4)−O(4)	2.525(5)
Na(2)−O(22)#5	2.375(5)	Na(4)−O(3)	2.549(4)
Na(1)···Na(3)	3.297(4)	Na(2)···Na(4)	3.289(4)
Na(1)···Cu(2)	3.177(2)	Na(2)···Cu(1)	3.521(2)
Na(1)···Cu(2)*	3.531(2)	Na(2)···Cu(1)*	3.184(2)
Na(3)···Cu(2)	3.197(3)	Na(4)···Cu(1)	3.193(3)
Na(3)···Na(3)*	3.440(4)	Na(4)···Na(4)*	3.434(4)

O(19)−Cu(1)−O(9)	173.6(2)	O(16)#5−Na(2)−O(4)	78.1(1)
O(19)−Cu(1)−O(6)	91.3(2)	O(22)#5−Na(2)−O(4)	71.0(2)
O(9)−Cu(1)−O(6)	91.8(2)	O(6)#5−Na(2)−O(4)	108.5(1)
O(19)−Cu(1)−O(12)	88.6(2)	O(9)−Na(4)−O(4)#6	166.9(2)
O(9)−Cu(1)−O(12)	88.8(2)	O(9)−Na(4)−O(16)#8	103.7(2)
O(6)−Cu(1)−O(12)	175.4(2)	O(4)#6−Na(4)−O(16)#8	87.2(2)
O(10)#5−Na(2)−O(19)	104.6(2)	O(9)−Na(4)−O(22)#8	109.8(2)
O(10)#5−Na(2)−O(16)#5	100.3(3)	O(4)#6−Na(4)−O(22)#8	78.8(2)
O(19)−Na(2)−O(16)#5	154.5(2)	O(16)#8−Na(4)−O(22)#8	80.0(2)
O(10)#5−Na(2)−O(22)#5	100.3(2)	O(9)−Na(4)−O(4)	80.6(2)
O(19)−Na(2)−O(22)#5	100.0(2)	O(4)#6−Na(4)−O(4)	90.2(2)
O(16)#5−Na(2)−O(22)#5	80.7(2)	O(16)#8−Na(4)−O(4)	167.2(2)
O(10)#5−Na(2)−O(6)#5	79.3(2)	O(22)#8−Na(4)−O(4)	87.2(2)
O(19)−Na(2)−O(6)#5	101.8(2)	O(9)−Na(4)−O(3)	80.1(1)
O(16)#5−Na(2)−O(6)#5	77.3(2)	O(4)#6−Na(4)−O(3)	89.7(1)
O(22)#5−Na(2)−O(6)#5	157.5(2)	O(16)#8−Na(4)−O(3)	108.4(2)
O(10)#5−Na(2)−O(4)	171.2(2)	O(22)#8−Na(4)−O(3)	165.6(2)
O(19)−Na(2)−O(4)	78.2(1)	O(4)−Na(4)−O(3)	84.1(1)

[a] Symmetry operations used to generate equivalent atoms: #5 $-x + 1$, $y + {}^1/_2$, $-z + {}^3/_2$, #6 $-x + 1$, $-y + 1$, $-z + 2$, #8 x, $-y + {}^1/_2$, $z + {}^1/_2$.

Results and Discussion

Synthesis. The complex initially formed in an aqueous solution containing 1-benzyl-4-acetato-1,4,7-triazacyclononane trihydrochloride, 2 equiv of $CuCl_2$, NaOH, and excess $NaCH_3COO$. It deposited when the filtrate was allowed to evaporate, following removal of the desired Cu(II) tacn derivative. To our surprise, an X-ray structure determination revealed that a new anionic Cu(II)−acetate complex had been

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Table 3. Hydrogen Bond Contacts for 1 (Å and deg)

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
O(21)−H(3)···O(2)#2[a]	0.998(10)	1.869(19)	2.839(5)	163(5)
O(21)−H(4)···O(18)	0.998(10)	1.83(3)	2.748(6)	152(6)
O(20)−H(15)···O(11)	0.65(6)	2.19(7)	2.816(8)	164(7)
O(18)−H(19)···O(12)	0.996(10)	1.91(4)	2.834(6)	154(7)
O(22)−H(1)···O(3)#1	0.66(6)	2.19(7)	2.836(6)	166(7)
O(22)−H(2)···O(20)	0.82(9)	1.96(9)	2.744(7)	159(8)
O(20)−H(20)···O(18)	0.66(8)	2.30(9)	2.859(7)	143(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y - {}^1/_2, -z + {}^3/_2$, #2 $-x, y + {}^1/_2, -z + {}^3/_2$.

obtained. Following this discovery, a higher yielding synthesis of **1** was designed. The reactions conditions represent a compromise between competing effects. It was found that higher proportions of copper(II) acetate returned copper(II) acetate as the crystalline phase, whereas lower proportions gave a light blue powdery product but failed to produce the blue crystalline phase. Heating in excess of 95 °C induced the formation of the light blue product prior to completing the addition of copper acetate. More dilute solutions returned Cu(II) acetate, as did removal of the light blue product prior to evaporation of the filtrate indicating that the light blue material is involved in the formation of **1**. The light blue material exhibited strong ν_{asym} (1572, 1524 cm^{-1}) and ν_{sym} (1431 cm^{-1}) acetate stretches. The spectrum is different from that of **1** or copper(II) acetate monohydrate. Elemental analyses corresponded to $\{[0.85Cu(OH)(CH_3COO)\cdot H_2O][0.15Cu(OH)_2]\}$; this can viewed as mixture of $[Cu(OH)CH_3COO)]$ and $Cu(OH)_2$. The analytical and spectroscopic data for **1** supported the proposed composition. In the IR spectrum, a water OH stretch is evident at 3467 cm^{-1} and pairs of ν_{asym} and ν_{sym} carboxylate stretches are evident at 1617 and 1583 cm^{-1}, and 1405 and 1344 cm^{-1}, respectively. The solution electronic spectrum of **1** was the same as that of Cu(II) acetate, both showing a broad band in the 750−800 nm region. The diffuse reflectance spectrum was different. It exhibited two of the three transitions expected for a square planar Cu(II) complex as broad bands in the 600−650 and 350−420 nm regions.

Structural Description. The molecular structure of $[Na_2Cu(CH_3COO)_4(H_2O)]\cdot H_2O$, **1**, exhibits two crystallographically unique but geometrically identical $[Na_2Cu(CH_3COO)_4(H_2O)]$ constructs (**A** for Cu(1) and **B** for Cu(2)) and two water molecules that participate in H-bonding interactions only (Figure 1). These two waters of hydration, O(18) and O(20), are the only components that give rise to the asymmetry that generates the two separate constructs. The other two water molecules, O(21) and O(22), are each coordinated to two sodium atoms and each donate H-bonds to a water and an acetate. All water hydrogen atoms were located in Fourier difference maps and refined with the exception of one on O(18).

In the anionic $[Cu(CH_3COO)_4]^{2-}$ complexes, four acetate anions coordinate to a square planar (SP) Cu(II) center and in turn bridge to one or more sodium ions through either one or both of their oxygen atoms. Cu−O bond lengths do vary (1.933(4) and 1.984(4) Å) but are in the expected range for carboxylates binding equatorially to Cu(II). The four acetates are arranged such that adjacent acetates lie on opposite sides of the plane defined by the copper coordination plane, probably to minimize steric interactions (Figure 2). The SP geometry is unexpected given the weak ligand field of acetate but has been observed in two $[Cu(betaine)_4]^{2+}$ complexes in which the ligands also adopt an up/down conformation. This complex is cationic as the betaine ligands are neutral, combining a negatively charged carboxylate with a positively charged quaternary ammonium.

Since the constructs are essentially identical, the discussion from hereafter focuses on construct **A**. The sodium atoms are in a distorted octahedral geometry defined by five acetate oxygen atoms and one water ligand (Figure 3) with Na−O distances in the 2.323(4)−2.771(5) Å range (Table 2). The acetates act as counterions and connect the symmetry-related

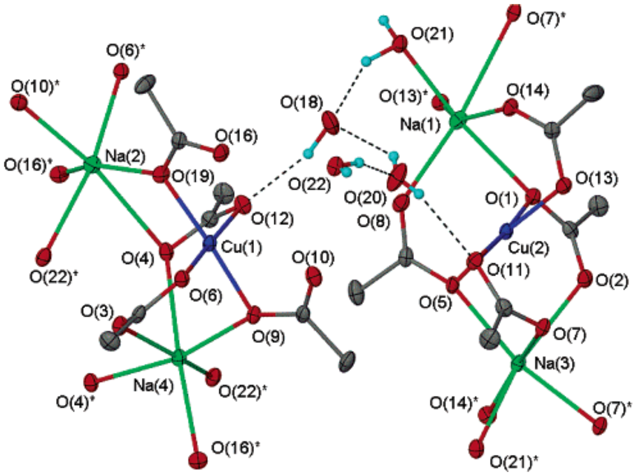


Figure 1. Asymmetric unit of **1** including oxygen atoms in the sodium coordination sphere. Hydrogen bonds (- - -). C and H atoms not labeled for clarity. H atoms on methyl and symmetry-related waters not shown.

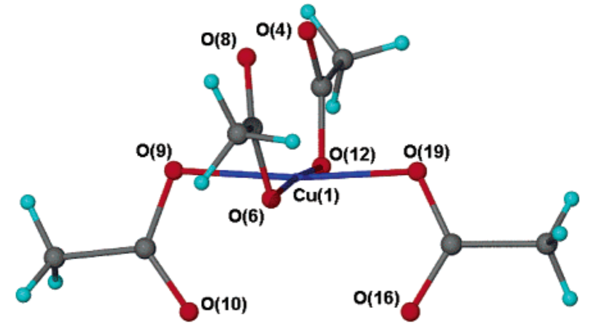


Figure 2. Square planar $[Cu(CH_3COO)_4]^{2-}$ anion in construct **A**.

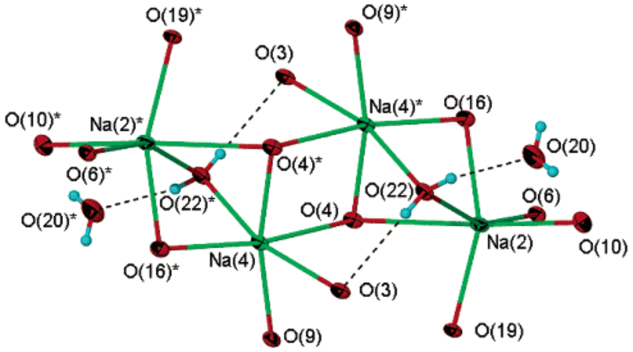


Figure 3. Coordination environment of sodium atoms in construct **A**. Asterisk (*) indicates symmetry-related atom.

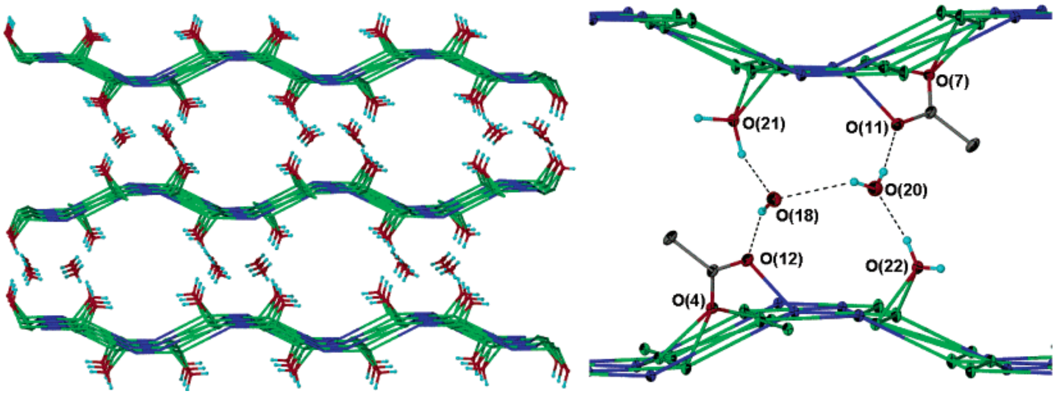
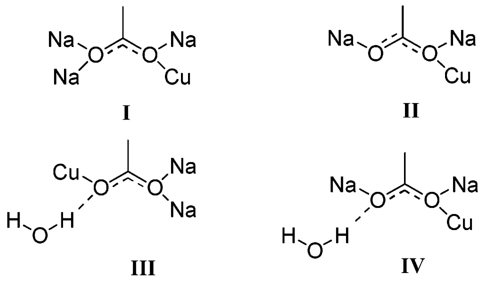


Figure 4. (a, left) Corrugated 2D sheets bridged by water molecules (viewed along *c* axis). Acetate groups and H-bonds have been removed for clarity. (b, right) The H-bonding network unit connecting the 2D sheets (viewed along *c* axis: bottom sheet, construct **A**; top sheet, construct **B**). Aside from the 2D sheets, the bridging waters and acetates from one asymmetric unit are shown. Na = green, Cu = blue, O = red, C = gray, H = light blue.

Chart 1. Coordination and Hydrogen-Bonding Modes (I−IV) for Acetate Anions in **1**



constructs. For each Na$^+$ center, four Na−O distances are below the sum of the van der Waals radii while the other two distances suggest weak Na$^+\cdots$O interactions. The longest contact of 2.78 Å is between Na(2) and an acetate oxygen, O(4). This oxygen atom is also involved in interactions with two other sodium atoms, Na(4) and Na(4)* (2.525(5) and 2.336(4) Å, respectively), the former representing the second weakest Na$^+\cdots$O interaction seen in the structure.

Constructs **A** and **B** self-assemble into two separate 2D sheets connected to one another through hydrogen bonds involving the uncoordinated water molecules (Figure 4a,b). One acetate and one sodium-bound water molecule per construct, respectively accept and donate H-bonds to the two uncoordinated water molecules that separate the sheets. The bridge can be broken down into three major groups of interactions: Na−O−H$\cdots$O−H$\cdots$O−Cu (sheet **B** to sheet **A**), Na−O−H$\cdots$(H)O−H$\cdots$O−Cu (sheet **A** to sheet **B**), and the O−H$\cdots$O contact between the uncoordinated waters (O(20)−H(20)$\cdots$O(18), 2.859(7) Å, 143(10)°) (see Figure 4b).

Within the 2D sheets, Cu and Na centers assemble via coordination to acetate and water into nanosized macrocyclic units consisting of six Na$^+$ and four Cu^{2+} with dimensions 0.9 × 1.2 nm. Each unit shares an edge with four macrocycles packing together into undulating sheets that lie atop each other 180° “out-of-phase”.

The acetates interact with the sodium, coppers and water in four different ways (Chart 1). Very recently the structure of Cu(CH$_3$COO)(CH$_3$O) provided the first example of acetate acting as a tetradentate ligand in a copper complex.[17] A substructure search of the CCDC revealed only two examples of acetate anions in a Cu/Na coordination environment in which the acetate anions in these structures exhibited only binding mode II.[11,12] Inclusion of carboxylates that are part of a larger ligand assembly revealed one structure, with a picolinate anion, that exhibited binding mode I.[7] No occurrences of modes I, III, or IV could be found in structures incorporating acetate anions.

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Supporting Information Available: X-ray crystallographic file for **1** in CIF format. This material is available free of charge from http://pubs.acs.org.

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