



**SERENDIPITOUS SYNTHESIS OF A Cu(OAc)₂ COMPLEX VIA
CuCl₂ CATALYZED OXIDATION OF 2-BUTANONE:
SYNTHESIS, CRYSTAL STRUCTURE, AND MAGNETIC
BEHAVIOR OF (5-NAP)₂(CH₃COO)₄Cu₂·nH₂O (n = 0 AND 2)
(5-NAP=2-AMINO-5-NITROPYRIDINE)**

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Keywords: copper complex, XRD, IR, magnetization.

A copper (II) catalyzed Baeyer-Villiger reaction of 2-butanone in the presence of oxygen and 2-amino-5-nitropyridine produced crystals of bis(2-amino-5-nitropyridine)tetraacetatedicopper(II) dehydrate, (**1**). **1** and its anhydrous form, (bis-2-amino-5-nitropyridine)tetraacetatedicopper(II), (**2**), were then synthesized directly from Cu(CH₃COO)₂·H₂O and 2-amino-5-nitropyridine. Crystals of both compounds were grown using slow evaporation, and characterized using IR, combustion analysis, X-ray powder diffraction, single crystal X-ray diffraction, and temperature-dependent magnetic susceptibility measurements. **1** and **2** are both monoclinic and crystallize in the space groups P2₁/c and C2/m, respectively. **2** exhibits 2-fold disorder in the 2-amino-5-nitropyridine molecule that arises due to symmetry. Both compounds pack in sheets of isolated dimers, and exhibit strong antiferromagnetic interactions within the dimers ($J = -442(5)$ and $-471(5)$ K for **1** and **2** respectively).

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INTRODUCTION

The structure and magnetic properties of copper(II) acetate monohydrate has been of interest in the magnetism community for over half a century. Guha¹ first observed the unexpected antiferromagnetic behavior of copper(II) acetate monohydrate in 1951 when he detected a decrease in magnetic moment that corresponded to a decrease in temperature. The precise physical and chemical phenomena explaining the magnetic properties of copper(II) acetate monohydrate were elucidated by Bleaney and Bowers² the following year; their experiments showed very strong antiferromagnetic coupling between isolated pairs of copper ions due to exchange interactions, thus explaining Guha's results. The magnetic and structural properties of copper II acetate monohydrate³ and its derivatives,^{4,5} have been closely studied to explain the findings of Bleaney and Bowers, as it was an early description of a compound with strong antiferromagnetic exchange.

Currently, we are involved in a project to synthesize and characterize copper coordination compounds of the type L₂CuX₂, where L is a substituted pyridine ligand and X is a halide ion. We have previously prepared members of this

family such as Cu(2-X-3CH₃py)₂X₂ (X=Cl, Br),⁶ Cu(2-amino-5-trifluoromethylpyridine)₂(X)₂ (X=Cl, Br),⁷ and Cu(2-amino-5-chloro-3-fluoropyridine)₂X₂ where (X=Cl, Br).⁸ In the course of our synthesis of Cu(2-amino-5-nitropyridine)Cl₂ (2-amino-5-nitropyridine=5-NAP), we serendipitously produced the compound (5-NAP)₂(CH₃COO)₄Cu₂·2H₂O (**1**). The previously unreported anhydrous form, (5-NAP)₂(CH₃COO)₄Cu₂ (**2**) was synthesized as well, through direct methods. It was determined that an unexpected reaction with 2-butanone produced acetate ions through Cu(II) catalyzed air-oxidation followed by hydrolysis. Here, we present the synthesis, crystal structure, and magnetic behaviors of both compounds and propose a reaction mechanism for the production of acetate ions from 2-butanone during the synthesis.

EXPERIMENTAL

Copper(II) chloride dihydrate was purchased from Allied Chemical Corporation. 2-Amino-5-nitropyridine (5-NAP) was purchased from Fluka Chemie, a subsidiary of Sigma Aldrich. Copper(II) acetate monohydrate was purchased from Matheson Coleman & Bell Corporation. 1-Butanol was purchased from Mallinckrodt, Inc. and 2-butanone was purchased from Alfa Aesar. All materials were used as received. IR spectra were recorded via ATR on a Perkin-Elmer Spectrum 100. X-Ray powder diffraction was carried out on a Bruker AXS-D8 Powder Diffractometer. Elemental analyses were carried out by Marine Science Institute, University of California, Santa Barbara, 93106.

Synthesis of (5-NAP)₂(OAc)₄Cu₂·2H₂O (1)

Compound **1** was previously synthesized by Yan and Wang.⁹

Method A: **1** was originally synthesized in an attempt to crystallize (5-NAP)₂CuCl₂, which has been characterized by IR, X-ray powder diffraction, single-crystal X-ray diffraction, and SQUID magnetometry.¹ 0.1032 g (0.250 mmol) of (5-NAP)₂CuCl₂ was dissolved in 45 mL of 2-butanone by heating to reflux, forming a clear, emerald green solution. The beaker was mostly covered and the solution was allowed to cool. Crystals began forming after seven days of slow evaporation. A mixture of large, dark green rectangular prisms with well defined-faces and a pale green crystalline solid were isolated by vacuum filtration, rinsed with cold 2-butanone, and allowed to air-dry. The two solids were separated manually and characterized by IR and combustion analysis. The odor of the filtrate indicated the presence of acetic acid. The dark green crystals proved to be (5-NAP)₂(OAc)₄Cu₂·2H₂O. The yield of **1** could not be calculated, because the pale green crystalline byproduct could not be completely separated. Only the larger crystals of **1** could be manually separated. The pale green crystalline solid has not been conclusively characterized at this time. For compound **1**: IR (ν in cm⁻¹): 3531 (vw), 3491 (vw), 3347 (vw), 3202 (vw), 1650 (m), 1624 (s), 1604 (s), 1574 (m), 1493 (w), 1431 (m), 1343 (m), 1296 (s), 1158 (vw), 1125 (w), 1078 (vw), 1010 (vw), 974 (vw), 847 (w), 833 (w), 767 (w), 687 (s), 625 (m), 577 (m), 544 (m). CHN found (calculated): C: 32.3 (31.9), H: 3.21 (3.88), N: 12.4 (12.4).

Method B: 1.00 mmol (0.1989 g) of Cu(CH₃COO)₂·H₂O was dissolved in 52 mL of 2-butanone by heating to 60 °C. A small amount of solid impurity was removed by filtration. In a separate beaker, 1.05 mmol (0.1463 g) of 5-NAP were dissolved in 20 mL of 2-butanone at room temperature. The two solutions were combined, stirred, and heated to 65 °C for 10 minutes before allowing the solution to cool to room temperature. Dark green rectangular prisms with well-defined faces formed on the bottom of the beaker after six days of slow evaporation (0.1149 g, 33.9 % yield). The IR spectrum was the same as that described in method A. The product was also shown to be the same as that from Method A via comparison of the powder X-ray diffraction pattern to the predicted spectrum from the single crystal data.

Synthesis of (5-NAP)₂(OAc)₄Cu₂ (2)

0.1996 g (1.000 mmol) of Cu(CH₃COO)₂·H₂O was dissolved in 50 mL of 1-butanol by heating to ~ 60 °C. 0.1465 g (1.05 mmol) 5-NAP was dissolved in 20 mL of 1-butanol by heating to ~ 50 °C. The 5-NAP solution was added to the copper acetate solution; the combined solution was stirred and heated until it reached 75 °C. The solution was allowed to cool and was partly covered. After 8 days of slow evaporation, small crystals with well-defined rectangular faces were harvested by vacuum filtration, washed with 1-butanol, and allowed to air dry. The crystals are dichroic; clover green and sky blue. Yield: 0.2225 g;

69.4 %. IR (ν in cm⁻¹): 3440 (w), 3352 (w), 3242 (vw), 1650 (m), 1626 (m), 1602 (s), 1573 (m), 1493 (w), 1429 (m), 1338 (s), 1295 (s), 1129 (w), 1015 (vw), 838 (w), 766 (w), 682 (m), 643 (vw), 625 (w), 539 (w), 521 (m). CHN found (calculated): C: 33.9 (33.7), H=3.32, (3.46) N=13.0 (13.1).

Table 1. X-Ray Data for **1** and **2**

	Compound 1	Compound 2
Empirical formula	C ₁₈ H ₂₆ Cu ₂ N ₆ O ₁₄	C ₁₈ H ₂₂ Cu ₂ N ₆ O ₁₂
Formula weight	677.55	641.50
Temperature	120(2) K	120(2) K
Wavelength	1.54178 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	C2/m
<i>a</i>	8.3062(3) Å	7.2797(3) Å
<i>b</i>	19.9736(7) Å	15.6618(5) Å
<i>c</i>	8.0082(3) Å	10.8921(3) Å
β	97.394(4)°	102.684(3)°
Volume	1317.55(8) Å ³	1211.55(6) Å ³
Z	2	2
Density (calculated)	1.708 Mg/m ³	1.758 Mg/m ³
Absorption coefficient	2.712 mm ⁻¹	2.849 mm ⁻¹
F(000)	692	652
Crystal size	0.17x0.16x0.06 mm ³	0.14x0.14x0.11 mm ³
θ range for data collection	4.43 to 74.50°	4.16 to 76.34°
Index ranges	-10 ≤ <i>h</i> ≤ 9; -13 ≤ <i>k</i> ≤ 24; -9 ≤ <i>l</i> ≤ 9	-9 ≤ <i>h</i> ≤ 9; -19 ≤ <i>k</i> ≤ 19; -13 ≤ <i>l</i> ≤ 13
Reflections collected	8602	10020
Independent reflections	2617	1317
Completeness to θ = 74.50°	[R _(int) =0.0535] 97.1 %	[R _(int) =0.0542] 99.4 %
Absorption correction	Semi-empirical from equivalents	Gaussian
Max. and min. transmission	1.00000 and 0.86607	0.812 and 0.714
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2617 / 0 / 195	1317 / 0 / 146
Goodness-of-fit on F ²	1.087	1.061
Final R indices [I > 2σ(I)]	R ₁ = 0.0350, wR ₂ = 0.0905	R ₁ = 0.0364, wR ₂ = 0.0948
R indices (all data)	R ₁ = 0.0402, wR ₂ = 0.0942	R ₁ = 0.0416, wR ₂ = 0.0993
Largest diff. peak and hole	0.427 and -0.660 e.Å ⁻³	0.411 and -0.462 e.Å ⁻³

¹ Bellesis, A. G., Turnbull, M.M., manuscript in preparation.

X-Ray Structure Analysis

Data for **1** and **2** were collected on an Agilent Technologies Gemini Eos CCD-Xray diffractometer using the CrysAlisPro software package with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) via ω -scans at 120(2) K employing a graphite monochromator. Cell parameters were determined and refined using CrysAlisPro¹⁰ and absorption corrections were made using SADABS.¹¹ The structure was solved by direct methods and refined via least-squares analysis using SHELXS97-2.¹² All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were added in calculated positions and refined using a riding model with fixed isotropic thermal parameters. The positions of hydrogen atoms bonded to nitrogen and oxygen atoms were located and refined anisotropically. Crystallographic information and details of the data collection can be found in Table 1.

Magnetic Susceptibility Data Collection

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Finely ground samples of the crystals were packed in gelatin capsules. The moment was measured using magnetic fields from 0 to 50 kOe at 1.8 K. Several data points were collected as the field was brought back to 0 kOe to check for hysteresis; none was observed. Magnetization was then measured from 1.8 to 310 K in a 1 kOe field. The contributions from the sample holder were measured independently and subtracted from the data set. The data was also corrected for the temperature independent paramagnetism of the Cu(II) ions ($60 \times 10^{-6} \text{ emu mol}^{-1} \text{Oe}^{-1}$ per ion) and for the diamagnetism of the constituent atoms ($-226.5 \times 10^{-6} \text{ emu mol}^{-1} \text{Oe}^{-1}$) estimated from Pascal's constants.¹³

RESULTS

Syntheses

Compound **1** was initially synthesized serendipitously in an attempt to recrystallize (5-NAP)₂CuCl₂ (Figure 1) from 2-butanone which yielded crystals of **1**.

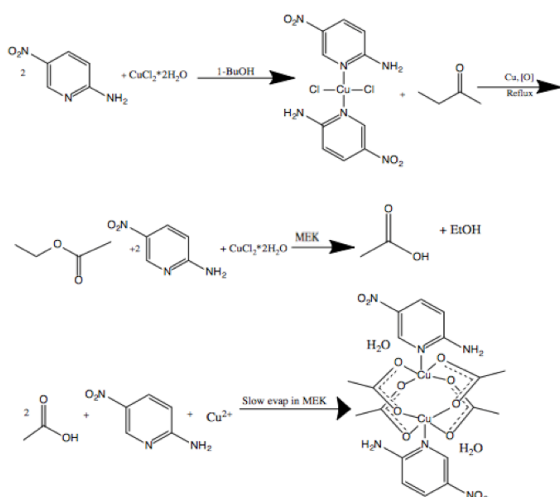


Figure 1. Proposed synthesis of **1**, via Method A.

A direct synthesis of **1** was then successfully carried out using copper(II) acetate monohydrate and 5-NAP in 2-butanone (Figure 2). Both synthesis techniques described here were previously unreported, as Yuan and Wang used a different pathway.⁹ When using 1-butanol as a solvent, the previously unreported anhydrous form, **2**, was synthesized (Figure 3).

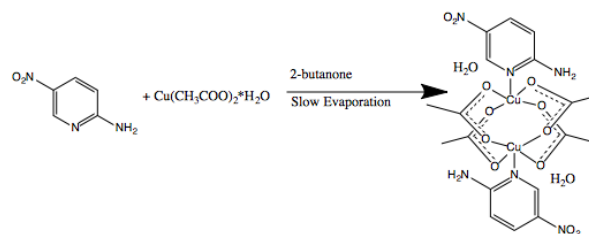


Figure 2. Method B for the synthesis of **1**.

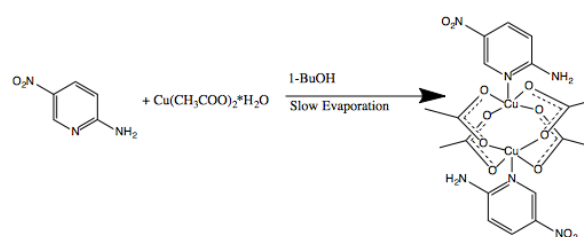


Figure 3. Synthesis of **2**

Crystal Structure

Compound **1** crystallizes in dimeric units in the monoclinic space group P2₁/c. The asymmetric unit comprises one Cu(II) ion, one coordinated 5-NAP molecule, two acetate ions, and one H₂O molecule. There is a crystallographic inversion center at (0,0,0) ($d_{\text{Cu}\dots\text{Cu}} = 2.6484(6) \text{ \AA}$) which generates the other half of the dimer (Figure 4). The copper coordination sphere has five-coordinate geometry in which the N-atom of the 5-NAP ring coordinates in the axial position. The Addison Parameter is $\tau = 0.0033$, indicating a very slightly distorted square pyramidal geometry.¹⁴ The continuous symmetry (CSM) parameter further quantifies the geometry;¹⁵ the CSM value for square pyramidal is 0.192, whereas the value for trigonal bipyramidal is 5.70 (a lower value indicates less distortion from the idealized geometry). Selected bond lengths and angles are given in Tables 2 and 3 respectively. All bond angles of **1** are unremarkable when compared to the previously published structure of **1**.⁹ The O-Cu-O angles are slightly distorted from the idealized 90 and 180 found in a perfect square pyramid, ranging from 88.53(8) to 90.24 and 167.85(7) to 168.05°, respectively. The 5-NAP molecule is canted by 8.16° relative to the Cu1-N1 bond making the C2-N1-Cu1 bond angle 128.68(16)° and the C6-N2-Cu1 bond angle 113.56(14)°.

When the crystal lattice of **1** is viewed parallel to the *a*-axis of the unit cell, it is seen to pack as stacked, pleated sheets (Figure 5). The sheets are held together by hydrogen bonding network between nitro group oxygen atoms, water molecules, and oxygen atoms on the acetate ions (Table 4). The amino group acts as a hydrogen bond donor through both -H-atoms, one of which bonds to an acetate oxygen

($d_{N2-H2A...O22\#1} = 2.855(3) \text{ \AA}$) and the other to a water molecule ($d_{N2...O1W\#2} = 2.903(3) \text{ \AA}$). The water molecules also act as hydrogen bond donors. One H-atom forms a H-bond to an acetate oxygen atom in an adjacent dimer ($d_{O1W-H1W...O12\#3} = 2.858(3) \text{ \AA}$); the other hydrogen atom forms a hydrogen bond to a nitro group oxygen atom on an adjacent dimer ($d_{O(1W)-H(2W)...O(1)\#4} = 2.859(3) \text{ \AA}$).

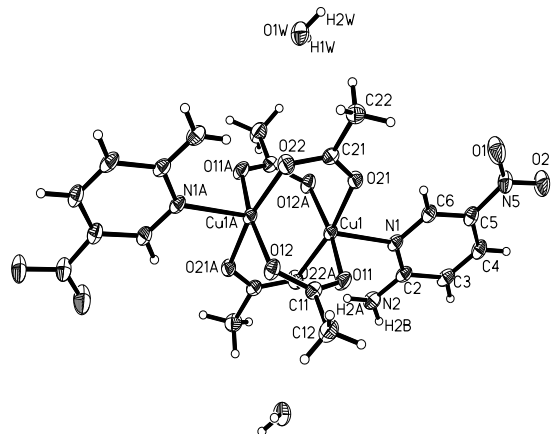


Figure 4. The thermal ellipsoid plot of the dimer of (1) showing 50% probability ellipsoids. Only the copper coordination sphere and the asymmetric unit are labeled for clarity.

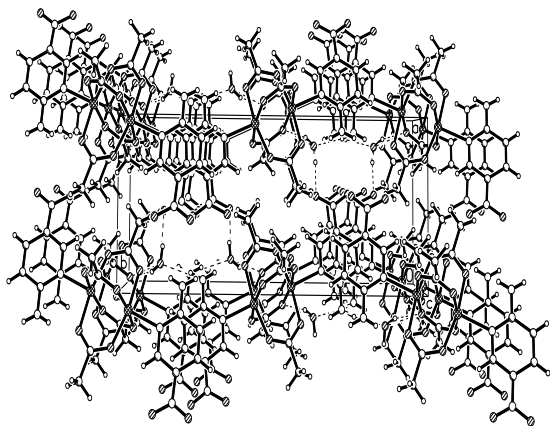


Figure 5. The unit cell of 1 viewed parallel to the *a*-axis, such that the origin is in the back right corner of the unit cell, shows how 1 packs in pleated sheets. Dotted lines show intermolecular H-bonding.

Compound (2) crystallizes in dimeric units, similar to 1, in the monoclinic space group *C2/m*. The 5-NAP molecule is canted due to steric interactions between neighboring 5-NAP molecules on adjacent dimers. The copper ion sits on a two-fold rotation axis with direction [0, 1, 0] at [0, *y*, 0]. An inversion center exists at the origin, equidistant between the two copper II ions ($d_{Cu...Cu} = 2.6047(8) \text{ \AA}$). The asymmetric unit comprises one bridging acetate ion, one copper (II) ion, and one 5-NAP molecule; the bridging tetraacetate dimer is produced through the combination of the inversion center and two-fold axis (Figure 6). The inversion center and 2-fold rotation axis produce the symmetry-equivalent 5-NAP

ring and copper II ion. Compound 2 exhibits static two-fold disorder in the 5-NAP molecule that arises due to a crystallographic mirror (Figure 7).

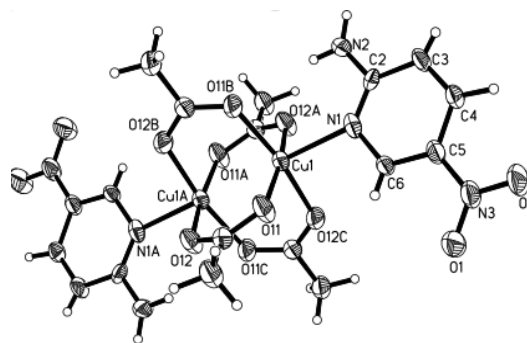


Figure 6. The thermal ellipsoid plot of (2) showing 50% probability ellipsoids. Only the copper coordination sphere and the asymmetric unit are labeled for clarity.

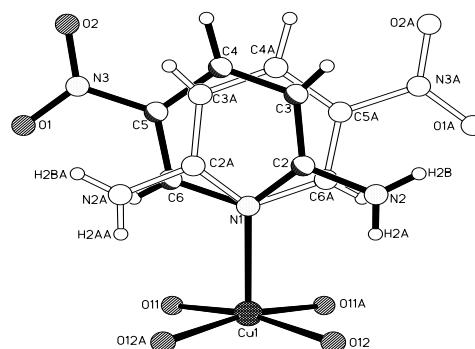


Figure 7. Two-fold disorder of the 5-NAP ring in 2. One position is shown as shaded spheres and solid bonds, while the other is shown as open spheres and hollow bonds.

The 5-NAP molecule is canted at an angle of 10.55° relative to the line of the Cu1-N1 bond; the mirror plane bisects N1, thus generating the disorder. In the discussion of the local structure, the 5-NAP ring will be restricted to one position because both positions are symmetry equivalent. The copper coordination sphere exhibits five-coordinate geometry. The symmetry operations require the Addison parameter to be exactly 0.00 and therefore it is not a helpful measure of the geometry. However, the CSM parameter has a value of 0.21 for a square pyramidal geometry and a value of 5.70 for a trigonal bipyramidal geometry. Therefore, 2 is best viewed as having a slightly distorted square pyramidal geometry around the copper ions. Selected bond lengths and angles are given in Tables 2 and 3, respectively. The O-Cu-O angles are slightly distorted from the idealized 90° and 180° found in a perfect square pyramid, ranging from $88.52(12)$ to $89.25(9)^\circ$ and $168.96(7)^\circ$, respectively. The C2-N1-Cu1 bond is $131.7(3)^\circ$ and the C6-N2-Cu1 bond is $111.6(3)^\circ$. 2 packs as flat sheets of isolated dimers held together by hydrogen bonding (Table 4) and, unlike 1, π -stacking (Figure 8). The lack of water molecules significantly limits the hydrogen bonding between layers. An amino group acts as an H-bond donor through one hydrogen which bonds to an adjacent nitro group oxygen atom ($d_{N2-H2B...O2\#5} = 2.957(7) \text{ \AA}$). The distance between the mean planes of the rings is $3.29(1) \text{ \AA}$ with a slip angle of $17.5(1)^\circ$ between the line connecting the ring centroids and the planes of the rings.

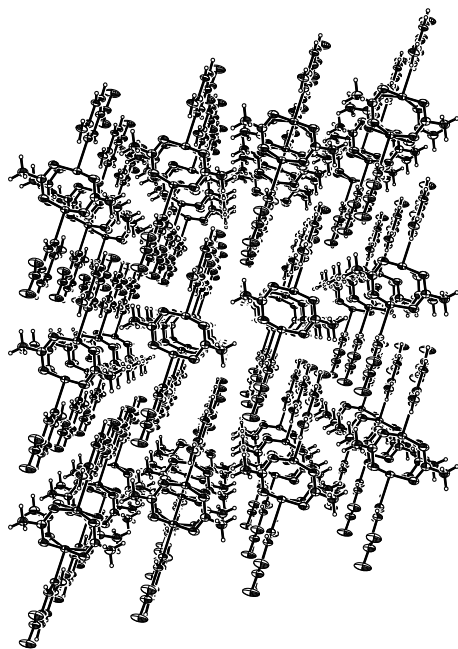


Figure 8. **2** viewed parallel to the b-axis. Sheets of isolated dimers interact through π stacking between 5-NAP molecules, and to a lesser extent through H-bonding between amino groups and nitro groups.

Table 2. Selected bond lengths

Compound 1		Compound 2	
Bond	Length (Å)	Bond	Length (Å)
Cu1...Cu1a	2.6484(6)	Cu1...Cu1a	2.6047(8)
Cu1-N1	2.2282(18)	Cu1-N1	2.214(3)
Cu1-O11	1.9633(18)	Cu(1)-O(11)	1.9672(17)
Cu1-O12a	1.9741(17)	Cu1-O12a	1.9687(17)
Cu1-O21	1.9652(16)		
Cu1-O22a	1.9642(17)		

Table 3. Selected bond angles

Compound 1		Compound 2	
Atoms	Angle (°)	Atoms	Angle (°)
C2-N1-Cu1	128.68(16)	C2-N1-Cu1	131.7(3)
C6-N1-Cu1	113.56(14)	C6-N1-Cu1	111.6(3)
O11-Cu1-N1	96.45(7)	O11-Cu1-N1	95.96(7)
O21-Cu1-N1	94.36(7)		
O22a-Cu1-N1	97.79(7)	O12-Cu1-N1	95.00(7)
O12a-Cu1-N1	95.40(7)		
O11-Cu1-O21	88.53(8)	O11-Cu1-O12c	89.25(9)
O11-Cu1-O22a	90.24(8)	O12a-Cu1-O12c	88.52(12)
		O11b-Cu1-O12c	168.96(7)
O22a-Cu1-O21	167.85(7)		
O11-Cu1-O12a	168.05(6)		
C2-N1-C6	117.71(19)	C2-N1-C6	116.6(6)
N1-C2-C3	121.5(2)	N1-C2-C3	126.7(7)
C2-C3-C4	119.9(2)	C2-C3-C4	117.5(6)
C3-C4-C5	117.7(2)	C3-C4-C5	118.7(5)
C4-C5-C6	120.3(2)	C6-C5-C4	119.3(6)
N1-C6-C5	122.8(2)	N1-C6-C5	121.2(7)

Symmetry Transformations to generate equivalent atoms for (1): #1 -x,-y+1,-z+2 For (2) #1 x,-y+1,z #2 -x+1,-y+1,-z #3 -x+1,y,-z #4 -x+1/2,-y+1/2,-z+1

Magnetic Data

Magnetic data for **1** and **2** were collected in a 0.1 T field from 1.8 K to 310 K. Data for **2** are shown in Figure 9. (Data for **1** are very similar) The data for both compounds were fit to the Bleaney-Bowers equation, where ρ represents a paramagnetic impurity, and $N\alpha$ represents the temperature independent paramagnetism (Eqn. 1).² The form of the Hamiltonian used was $H = -J^2 S_1^* S_2$. The data were fit per mole of dimer.

In **1**, the best fit yielded $J = -442(5)$ K, Curie constant = $1.09(16)$ emu(K) mol(Oe)⁻¹, and $\rho = 1.70(10)$ %. In **2**, the best fit yielded $J = -471(5)$ K, Curie constant = $0.970(16)$ emu(K) mol⁻¹(Oe)⁻¹, and $\rho = 1.62(10)$ %. In each **1** and **2**, χ reaches a maximum near 278 K (**1**), or 294 (**2**). As the temperature decreases, the susceptibility steadily decreases as a result of the antiferromagnetic interactions, until near 77 K (**1** and **2**) where the dimer is in the singlet state and only trace impurities contribute to the moment. At temperatures below 77 K, the χT value remains constant as would be expected for a sample with a small paramagnetic impurity.

The magnetization was measured at a constant temperature of 1.8 K in a field varying from zero to 50 kOe. For a Cu(II) ion, a saturation magnetization near 6000 emu mol⁻¹ is expected.¹³ The saturation magnetization was 100 emu mol⁻¹ (**1**) and 45 emu mol⁻¹ (**2**). Saturation magnetization of this magnitude is in agreement with the presence of a small paramagnetic impurity with the bulk sample in a singlet state. A small increase in moment at 50 K in both compounds indicates the presence of a trace of O₂.

$$\chi_m = \frac{2N\beta^2 g^2}{3kT} \left[1 + \frac{1}{3} \exp\left(-\frac{2J}{kT}\right) \right]^{-1} (1 - \rho) + \frac{N\beta^2 g^2 \rho}{4kT} + N\alpha$$

Equation 1. The Bleaney-Bowers Equation

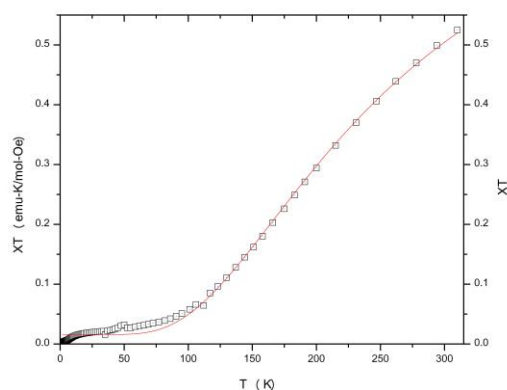


Figure 9. $\chi_m T$ vs. T plot for **2** in a 0.1 T field. The solid line represents the best fit to a dimer model with a paramagnetic impurity term.

Table 4. Hydrogen-bonding of **1** and **2**.

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA)
1				
N2-H2A...O22 #1	0.85(3)	2.02(4)	2.855(3)	165(3)
N2-H2B...O1W #2	0.87(3)	2.05(3)	2.903(3)	170(3)
O1W-H1W...O12 #3	0.85(4)	2.04(4)	2.858(3)	162(3)
O1W-H2W...O1 #4	0.88(4)	2.00(4)	2.859(3)	168(3)
2				
N(2)-H(2B)...O(2)#5	0.82(7)	2.14(7)	2.957(7)	171(6)

Symmetry transformations to generate equivalent atoms for (**1**): #1 -x,-y+1,-z+2; #2 -x,y-1/2,-z+3/2; #3 x,y,z-1; #4 -x+1,-y+1,-z+1. For (**2**) #1 x,-y+1,z #2 -x+1,-y+1,-z #3 -x+1,y,-z #4 -x+1/2,-y+1/2,-z+1 #5 -x+1/2,y+1/2,-z+1

DISCUSSION

Copper(II) is known to act as a Baeyer-Villiger catalyst capable of oxidizing ketones to esters¹⁶ and lactones¹⁷ in the presence of molecular oxygen. Punniyamurthy and Rout have recently written a review on copper-catalyzed oxidation.¹⁸ Other transition metal complexes, including platinum-, iron-, and nickel-based systems, have been widely studied as well.¹⁹ A Baeyer-Villiger reaction occurs when the ketone is protonated and then undergoes a nucleophilic attack by an oxygen species, forming the "Criegee intermediate."²⁰ This unstable species allows for the insertion of an oxygen atom next to the carbonyl group, forming an ester²¹⁻²³. The Cu(II) serves the role of a Lewis acid in this reaction and must coordinate to carbonyl oxygen atom. The structure of the catalytic complex is likely to be Cu(5-NAP)_xCl_y(2-butanone) although this has not been demonstrated. If water is present, hydrolysis can subsequently occur, forming a carboxylic acid and an alcohol (acetic acid and ethanol in this instance) which provides the necessary acetate ions for the formation of **1**.

Compounds **1** and **2** have strong local structural similarities, despite having different space groups and thus different symmetry. The greatest difference in the local structures between the two compounds is the existence of disorder in **2**. However, there are nuanced differences between the two structures, and some considerable differences appear when they are compared to known crystal structures of similar, previously reported Cu(II) carboxylate dimers. The O-Cu-O angles are unremarkable when compared to the published structure of copper acetate monohydrate.³ In compounds **1** and **2**, the bond lengths in the copper coordination sphere are within experimental error compared to the Cu-O and Cu-N bonds found in bis(pyridine)tetraacetatedicopper(II)²⁴ and less than 0.03 Å different than the Cu-O bonds in copper (II) acetate monohydrate.³ Each analogous bond in **1** and **2** in the copper coordination sphere is the same length within experimental error. The distance between the Cu(II) ions in each dimer, 2.648(4) Å in **1** and 2.605(8) Å in **2**, are distinctly different, but are comparable to the Cu-Cu distances in bis(pyridine)tetraacetate-dicopper(II) which is 2.641 Å and in copper(II) acetate monohydrate, which is 2.616 Å. It is unclear why the Cu...Cu distance differs so greatly between **1** and **2**, although differences in packing are almost certainly important.

Analogous bond angles differ greatly between compounds **1** and **2** and show distortion, especially in the case of **2**. The C6-N1-Cu1 and C2-N1-Cu1 bonds are distorted away from 120° in both compounds due to the steric hindrance provided by the amino group present at the 2-position in 5-NAP. The steric hindrance between the acetate ions and the amino group causes the 5-NAP molecule to be canted relative to the Cu-N bond, and therefore the C2-N1-Cu1 is larger than 120°. The C6-N1-Cu1 bond is distorted an equal amount less than 120° in both **1** and **2** in order to compensate and distribute the steric strain. The C2-N1-Cu1 bond angle in both **1** and **2** is larger than the analogous bond angle in bis(pyridine)-tetraacetatedicopper(II) by 7.5° and 10.5°, respectively.²⁴ The pyridine molecule is not canted because there is no unsymmetrical steric hindrance, unlike in the 5-NAP compounds, and therefore the Cu-N-C bonds are both 121.5°. The bond angles of the 5-NAP ring in **1** do not differ from the published crystal structure of 5-NAP by more than 1.4°. ²⁵ However, in **2**, the N(1)-C(2)-C(3) bond is 3.7° larger than the crystal structure of pure 5-NAP, and is 5.2° larger than the analogous angle in **1**.

The magnetic behavior of **1** and **2** was unsurprising. Copper acetate compounds and their derivatives have long been known to exhibit very strong antiferromagnetic interactions.^{1,2} The exchange constants reported for Cu(II) acetate monohydrate²⁶ and pyridine²⁷ complexes are comparable to those observed here with values of $2J = -409$ and -466 K respectively.

In conclusion, we have observed the Cu(II)-catalyzed Baeyer-Villiger oxidation of 2-butanone to produce acetate ions and ethanol. Cu(II) and 5-NAP coordinated to the acetate ions, forming bis-5-NAPtetraacetatecopper(II) which was also prepared by direct synthesis along with its anhydrous analogue. Both compounds crystallize in a monoclinic space group, and the anhydrous compound exhibits static disorder of the 5-NAP. Both compounds form isolated dimers, leading to strong antiferromagnetic interactions.

ACKNOWLEDGEMENTS

Financial assistance from the NSF (IMR-0314773) and the Kresge Foundation toward the purchase of the MPMS-XL SQUID magnetometer are greatly appreciated.

The Bruker D8-Advance powder X-ray Diffractometer was purchased with the assistance of funds from the Kresge Foundation and PCI Synthesis, Inc. AGB would like to thank PCI Synthesis, Inc. and the Clark University LEEP Center for a Summer Research Fellowship.

APPENDIX.

Supplementary Data: CCDC (1049172) and CCDC (1026255) contain the supplementary crystallographic data for 1 and 2, respectively. This data can be obtained free of charge via from <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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- ¹Guha, B. C., *Proc. Roy. Soc. A.*, **1951**, 206, 353.
- ²Bleaney, B., Bowers, K. D., *Phil. Mag.*, **1952**, 214, 451.
- ³de Meester, P., Fletcher, S. R., Skapski, A. C., *J. Chem. Soc., Dalton Trans.* **1973**, 23, 2575.
- ⁴Yamanaka, M., Uekusa, H., Ohba, S., Saito, Y., Iwata, S., Kato, M., Tokii, T., Muto, Y., Steward, O. W., *Acta Crystallogr B.* **1991**, B47, 344.
- ⁵Cruz-Enriquez, A., Baez-Castro, A., Hopfl, H., Parra-Hake, M., Campos-Gaxiola, J. J., *Acta Crystallogr E.*, **2012**, 68, 339.
- ⁶Herringer, S. N., Turnbull, M. M., Landy, P. L., Wikaira, J. L., *J. Chem. Soc., Dalton Trans.*, **2011**, 40, 4242
- ⁷Forman, R. L., Gale, A. J., Landee, C. P., Turnbull, M. M., Wikaira, J. L., *Polyhedron*, **2015**, 89, 76.
- ⁸Solomon, B. L., Landee, C. P., Turnbull, M. M., Wikaira, J. L., *J. Coord. Chem.*, **2014**, 67, 3953.
- ⁹Yuan, Q., Wang, X., *Chem. Res.*, **2006**, 17, 24.
- ¹⁰CrysAlisPro Oxford Diffraction Ltd., Version 1.171.35.19 (release 27-10-2011 CrysAlis171.NET).
- ¹¹Sheldrick, G. M., SADABS v 2.01: An empirical absorption correction program, Bruker AXS Inc., Madison, WI (**1999**).
- ¹²Sheldrick, G. M., *Acta Cryst. A* **2008**, 64, 112.
- ¹³Carlin, R. L., *Magnetochemistry*, Springer-Verlag, **1986**.
- ¹⁴Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J., Verschoor, G. C., *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
- ¹⁵a)Pinsky, M., Avnir, D. *Inorg. Chem.* **1998**, 37, 5575; b) Landry, B. R.,Turnbull, M. M., Twamley, B., *J. Chem. Crystallogr.*, **2007**, 37, 81.
- ¹⁶Szpakolski, K. B., Latham, K., Rix, C. J., White, J. M. *Inorg. Chim. Acta.*, **2011**, 376, 628.
- ¹⁷Zang, J., Ding, Y., Yan, L., Wang, T., Gong, L., *Catal. Commun.* **2014**, 51, 24.
- ¹⁸Punniyamurthy T., Rout, L., *Coord. Chem. Rev.*, **2008**, 252, 134.
- ¹⁹Strukel, G., *Angew. Chem. Int. Ed.*, **1998**, 37, 1198.
- ²⁰Criegee, R., *Justus Liebigs Ann. Chem.*, **1948**, 560, 127.
- ²¹Reyes, L., Alavarez-Idaboy, J. R., Mora-Diez, N., *J. Phys. Org. Chem.*, **2009**, 22, 643.
- ²²Krow, G. R., *Org. Reactions*, **2004**, 251.
- ²³Michelin, R. A., Sgarbossa, P., Scarso, A., Strukul, G., *Coord. Chem. Rev.* **2010**, 254, 646.
- ²⁴Uekusa, H., Ohba, S., Saito, Y., Kato, M., Tokii, T., Muto, Y., *Acta Crystallogr. C.* **1989**, C45, 377.
- ²⁵Aakeroy, C. B., Beatty, A. M., Nieuwenhuyzen, M., Min Zou, *J. Mater. Chem.*, **1998**, 8, 1385.
- ²⁶Emali, A., *Turk. J. Phys.*, **2000**, 24, 667.
- ²⁷ Muto, Y., Tokii, T., Chijiwa, K., Kato, M., *Bull. Chem. Soc. Jpn.*, **1984**, 57, 1008.

Received: 12.02.2014.
Accepted: 07.03.2015.