

# NaH[Cu<sub>2</sub>(O<sub>2</sub>C<sub>2</sub>H<sub>3</sub>)<sub>6</sub>]: A New Compound Containing Copper-to-Copper Bonding

T. Siegrist,\* B. L. Chamberland,† A. P. Ramirez,\* and R. LoBrutto‡

\*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974; †Department of Chemistry and Biochemistry, Tempe, Arizona 85287; and ‡Department of Botany, Arizona State University, Tempe, Arizona 85287

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DEDICATED TO THE MEMORY OF ALEXANDER F. WELLS

While attempting the synthesis of the mineral diabolite Pb<sub>2</sub>CuCl<sub>2</sub>(OH)<sub>4</sub> via a gel growth method, a new and interesting copper compound was isolated. The slow crystal growth of this new blue compound was generated from silica gel acidified with acetic acid. The crystals grew in the gel for over a period of one year. Attempted characterization using the X-ray powder technique indicated the crystals to be a new phase and not that of the mineral diabolite. Single-crystal studies were carried out and a new structure was obtained. The structure is based on square pyramidal complexes of copper in which the two pyramids interact through Cu–Cu bonds. Its chemical composition was deduced to be NaH[Cu<sub>2</sub>(O<sub>2</sub>C<sub>2</sub>H<sub>3</sub>)<sub>6</sub>]. The structure is similar to that found in the classical copper acetate dimer which possesses unusual magnetic properties. Its synthesis, chemical characterization, and structure is described. The space group for this new copper dimer is *I*2/a, *Z* = 4, with unit cell parameters *a* = 8.145(2) Å, *b* = 17.828(3) Å, *c* = 13.531(2) Å, and  $\beta$  = 98.70(2)°. © 1996 Academic Press, Inc.

## INTRODUCTION

Diabolite, a complex mineral of copper and lead, was originally found in lead mines of Somerset, England. It is also observed in other locations (e.g., Mammoth Mine, in Arizona) and has recently been successfully prepared in the laboratory. The mineral was first studied by Spencer and Mountain (1). They determined the mineral composition, Pb<sub>2</sub>CuCl<sub>2</sub>(OH)<sub>4</sub>, on an exceedingly small amount of pure sample. The structure of the mineral was later determined by Palache using a sample from Arizona. Details of its crystal structure include its space group, *P*4mm, tetragonal, with unit cell parameters *a* = 5.83 Å and *c* = 5.46 Å (2). In 1951 the mineral structure was reexamined by Byström and Wilhelmi (3) and they arrived at the same structural details and conclusions as Palache. The synthesis and thermal stability study of diabolite was carried out by Winchell and Wenden (4) using both ambient pressure and hydrothermal conditions. The synthesis that intrigued us

was the slow diffusion technique wherein a solution of CuCl<sub>2</sub> · 2H<sub>2</sub>O was allowed to diffuse through the walls of a cracked test tube into a hydrous bath of Pb(OH)<sub>2</sub> in order to generate the mineral. The experimental conditions given for the highest yields of diabolite were 25°C and 339 days.

It is interesting to note that Wells devoted much of the classic text “Structural Inorganic Chemistry” (5) to copper structural chemistry. To illustrate this point, Chapter 25 of the book contains the structural chemistry of copper, silver, and gold. Forty-six pages of the 52-page chapter are dedicated to copper, or contains mention of that element or its ions (88% of the chapter). In fact, within Part II of the text, Chapter 25 is surpassed (in terms of total number of pages) by only two chapters, on Group VIII and other transition metals (Chapter 27), and on silicon (Chapter 23). The 46 pages in Chapter 25 devoted to copper chemistry covers more space than the elements (or groups) mentioned in 14 other chapters found in Part II of the book. The structural chemistry of this single elements is equaled, however, by two other Chapters (a total of 48 pages each)—S, Se, and Te (Chapter 16) and boron (Chapter 24). To have known Wells personally would also support the contention that he was fascinated with the crystal chemistry of the element Cu. Any publication on the subject of copper interested him. Personally, he published at least four seminal structural papers on copper compounds. These include the compounds CsCuCl<sub>3</sub> and CuCl<sub>2</sub>, and the minerals atacamite, Cu<sub>2</sub>(OH)<sub>3</sub>Cl, and malachite, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>.

## EXPERIMENTAL

The long time involved with the diabolite crystal growth led one of the authors (B.L.C.) to repeat the growth experiment during a sabbatical leave. Since a proper cracked test tube was not readily available, it was decided to use a normal U-tube as a gel-growth container. Silica glass, acidi-

fied with acetic acid, formed a gel which was used as the medium instead of the hydrous bath. A U-tube, partially filled with water glass and treated with glacial acetic acid to form a silicate gel. After the gel had formed, a copper(II) chloride hydrate solution was added to one arm of the cell, and lead(II) acetate solution was placed into the other side. The tube was sealed off with corks and allowed to remain undisturbed at room temperature for a period of 375 days. After some 200 days, large blue crystals in the form of cubes and octahedra were noted in the gel, but these were not disturbed. After a total of 400 days there were no appreciable changes in the U-tube apparatus and the system was opened to isolate the blue crystals. These crystals were found to be acid and water soluble, yielding a blue solution (royal purple in the presence of ammonia), indicative of the cupric ion. The crystals, when exposed to air for a long period of time, would lose acetic acid and become white and opaque via an efflorescent process. The larger crystals, however, were more resistant to efflorescence and they maintained their shape and color for about a year while kept in a vial under a self-generated vapor of acetic acid.

X-ray studies on the powdered crystals showed a busy pattern which did not match diabolite or any other copper mineral listed in the ICDD Powder Diffraction File (6). A qualitative analysis showed the presence of copper as the amino complex, and faint traces of  $\text{Cl}^-$  and  $\text{Pb}^{2+}$  ions. The gel also yielded white opaque crystals which were identified by X-ray powder diffraction techniques to be  $\text{PbCl}_2$  or cotunnite. In fact, some blue crystals even contained this phase as an intergrowth. No test for the sodium ion was carried out initially, but the electron density obtained from the X-ray data was consistent with a sodium ion on what was previously assumed to be a  $\text{Pb}^{2+}$  site. Further investigations using energy-dispersive X-ray analysis confirmed the presence of sodium and the absence of lead in the blue crystals. Water (or silica) glass is an aqueous solution of silica in concentrated NaOH which offers a rich source for sodium ions for the crystal growth.

The quantitative weight loss at 100°C after one day indicated a 1.75% weight loss. A major change in the X-ray powder pattern was noted with the production of a new phase. At 300°C in air for 2 hours, a weight loss of 57% occurred. The residue appeared as a black "molten" mass and the X-ray powder techniques revealed the presence of moderate amounts of Cu,  $\text{Cu}_2\text{O}$ , and a trace of  $\text{CuO}$ . The theoretical weight loss with the production of  $\text{Cu}_2\text{O}$  is 71.7%.

Data for a single-crystal structure analysis were collected using a Enraf-Nonius CAD-4 single-crystal diffractometer with graphite-monochromatized  $\text{MoK}\alpha$  radiation controlled by the NRCCAD program (7). All subsequent calculations were carried out on a SUN workstation using the NRCVAX program suite (8). A Gaussian integration

TABLE 1  
Crystallographic Data of  
 $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$

Space group	<i>I</i> 2/a
Z	4
<i>a</i> [Å]	8.145(2)
<i>b</i> [Å]	17.828(3)
<i>c</i> [Å]	13.531(2)
$\beta$ [°]	98.70(2)
Volume [Å <sup>3</sup> ]	1942.2(6)
Calculated density [gr/cm <sup>3</sup> ]	1.725
Absorption coefficient $\mu$ [mm <sup>-1</sup> ]	3.36
$2\Theta_{\text{max}}$ [°]	80
Measured reflections	23590
Unique reflections	6014
Observed reflections ( $I > 2.5\sigma(I)$ )	4251
Merged <i>R</i> -value on intensities	0.034
Minimum transmission	0.376
Maximum transmission	0.496
Number of parameters	152
<i>R</i> <sub>F</sub> (observed)	0.030
<i>R</i> <sub>w</sub> (all)	0.051
<i>R</i> <sub>w</sub> (observed)	0.045
Goodness of fit	1.16
Secondary extinction [ $\mu\text{m}$ ]	0.097(6)

absorption correction was applied to the measured intensities. Results are given in Tables 1 and 2, and selected bond distances are shown in Table 3. A view of the copper coordination is shown in Fig. 1.

## RESULTS AND DISCUSSION

The crystal structure  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$  contains square pyramidal copper, with Cu–O distances within the pyramidal plane ranging from 1.954 to 1.978 Å, the distance to the apical oxygen being 2.169 Å. These distances are consistent with those found in other pyramidal Cu–O coordinations. A second pyramid, related by a center of symmetry, is attached to the first via four bidentate acetate groups. This produces a short contact to the other copper ion in the basal plane of the pyramid, of only 2.591 Å, close to the copper–copper distance found in metallic copper, of 2.56 Å. This arrangement of two pyramidal copper ions is identical to the one found in the "classical" copper dimer, copper acetate [9], where the copper–copper distance is 2.64 Å, only slightly longer than distance found in  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$ . The distance to the next copper ion is rather large, 7.05 Å, indicating that the copper pairs are quite well isolated from other pairs. The sodium coordination polyhedron is a distorted octahedron, with distances ranging from 2.38 to 2.413 Å. Since this octahedron is large enough to accommodate a  $\text{Pb}^{2+}$  ion, an occupancy refinement was carried out to test for the possible presence of lead on this particular site. However, the refined value was within three sigmas of the electron density for sodium.

**TABLE 2**  
**Atomic Positions of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$** 

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}$ [ $\text{\AA}^2$ ]	occ
Cu	0.16584(3)	0.194158(14)	0.207032(19)	1.930(7)	
Na	1/4	0.10468(7)	0	2.27(4)	
O1	0.50500(22)	0.27780(11)	0.21289(14)	2.99(6)	
O2	0.36023(22)	0.18297(10)	0.13653(13)	2.77(6)	
O3	0.0739(3)	0.26908(11)	0.10780(15)	3.39(7)	
O4	0.2201(3)	0.36498(10)	0.18121(14)	3.19(7)	
O5	0.05858(22)	0.09937(9)	0.11960(12)	2.46(5)	
O6	0.4321(3)	0.00660(12)	0.07367(16)	4.26(9)	
C1	0.4890(3)	0.22273(13)	0.15457(15)	2.16(6)	
C2	0.6340(3)	0.20294(20)	0.10328(22)	3.29(10)	
C3	0.1143(3)	0.33686(14)	0.11407(18)	2.78(8)	
C4	0.0303(6)	0.38903(23)	0.0346(3)	5.04(17)	
C5	0.9702(3)	0.04603(12)	0.13705(17)	2.47(7)	
C6	0.9053(6)	0.03963(21)	0.2339(3)	4.48(14)	
H1	0.732(7)	0.221(3)	0.137(4)	8.6(5)	
H2	0.648(7)	0.155(3)	0.105(4)	8.6(5)	
H3	0.613(7)	0.216(3)	0.040(4)	8.6(5)	
H4	0.061(7)	0.435(3)	0.043(4)	8.6(5)	
H5	0.504(7)	0.368(3)	0.024(4)	8.6(5)	
H6	0.577(7)	0.391(3)	-0.043(4)	8.6(5)	
H7	0.807(7)	0.047(3)	0.223(4)	8.6(5)	
H8	0.106(7)	0.495(3)	0.248(4)	8.6(5)	
H9	0.562(7)	0.428(3)	0.221(4)	8.6(5)	
H10	0.001(7)	-0.001(3)	0.013(4)	8.6(5)	0.5

Note.  $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.

**TABLE 3**  
**Selected Interatomic Distances in  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$** 

Cu	Cu	2.5911(6)
	Na	3.3827(8)
	O1	1.954(2)
	O2	1.978(2)
	O3	1.960(2)
	O4	1.959(2)
Na	O2	2.380(2)
	O5	2.413(2)
	O6	2.409(3)
C1	O1	1.254(3)
	O2	1.259(3)
	O2	1.500(4)
C3	O3	1.251(4)
	O4	1.258(4)
	C4	1.505(4)
C5	O5	1.237(3)
	O6	1.277(3)
	C6	1.490(4)

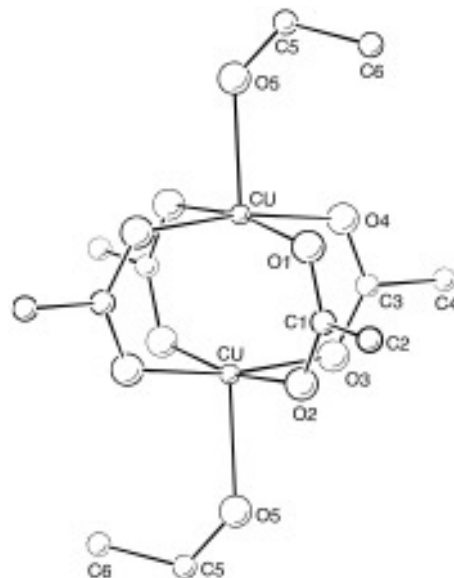


FIG. 1. Double pyramid of copper, joined by acetic acid at their respective basal planes.

The magnetic susceptibility of a crystal of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$  was measured as a function of temperature in a field of 1 kG, using a Quantum Design SQUID magnetometer. The data are displayed in Fig. 2. At low temperature, a Curie tail is evident, probably due to small amounts of decomposed  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$ . The magnetic moment expected from the  $\text{Cu } ^2\text{D}_{5/2}$  state is quenched, due to the copper-copper interaction. This behavior is analog to the one observed in copper acetate (10). The lowest energy level for the two copper ions splits into a nonmagnetic singlet and a paramagnetic triplet, the latter is then further split in a magnetic field. This accounts for the increase of the magnetic susceptibility, with a maximum

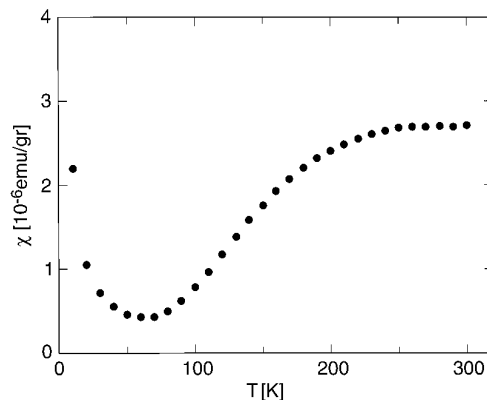


FIG. 2. Temperature dependence of the magnetic susceptibility of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$ .

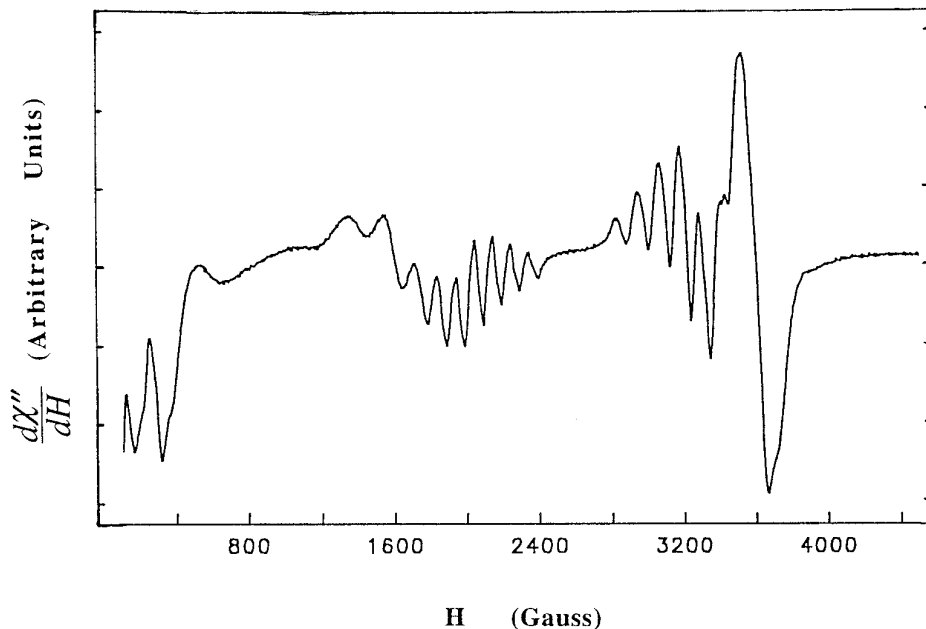


FIG. 3. Electron paramagnetic resonance (EPR) spectrum of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$ , recorded at 125 K.

around 300 K, giving an approximate exchange energy of 480 K, close to the values found in copper acetate.

A preliminary EPR study was carried out on a single crystal of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$ . At 125 K, at an arbitrary orientation with respect to the DC magnetic field, at least three separate spectral regions are apparent (Fig. 3), one near zero field, another near 2000 Gauss, and finally one in the 2800–3700 Gauss range (near the free-electron region of  $g = 2$ ). Each feature exhibits substantial hyperfine structure, attributable to the  $^{63,65}\text{Cu}$  nuclei, each with spin  $I = 3/2$ . There is evidence in both the mid- and high-field features of seven-line splittings with intensity ratios of 1:2:3:4:3:2:1. This would be expected for two structurally equivalent copper atoms if the magnetic field were oriented along some crystallographic axis. Similar splittings were observed by Bleaney and Bowers (11) in the copper acetate dimer, but in the present case, the splittings are somewhat greater (100–110 G vs 70 G for copper acetate). A detailed analysis of the EPR properties of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$  will be presented elsewhere. Consistent with the susceptibility data, the EPR spectrum of the same crystal at 4.2 K has essentially the same features.

## CONCLUSIONS

Double salts of alkali metal cations complexed with copper acetate anions have been known for at least one cen-

tury. The preparation of  $M_4\text{Cu}(\text{O}_2\text{C}_2\text{H}_3)_4$ , where  $M = \text{Li}^+$ ,  $\text{Rb}^+$  or  $\text{NH}_4^+$ ,  $\text{K}_2\text{Cu}(\text{O}_2\text{C}_2\text{H}_3)_4$ ,  $\text{RbCu}(\text{O}_2\text{C}_2\text{H}_3)_3$ , and  $(\text{NH}_4)\text{Cu}(\text{O}_2\text{C}_2\text{H}_3)_3$  (some of these salts possess acetic acid as solvate molecules) has been reported by Hardt and Street (12). It is interesting to note, however, that all their attempts to prepare the sodium analog failed. The structures of the isolated double salts were not investigated but their X-ray powder patterns have been reported. It is possible that some of these double salts may possess dimer units like those found in our product.

The isolation of  $\text{NaH}[\text{Cu}_2(\text{O}_2\text{C}_2\text{H}_3)_6]$  was unexpected and its structure was unanticipated. The synthesis of diabolite seemed straightforward, though happenstance. Our starting reagents were essentially the same as those used by Winchell and Wenden but the reaction container was somewhat more elaborate. The conditions and reaction times were comparable in the two experiments. The products, however, were radically different. In our system the  $\text{Cl}^-$  ions were eventually captured by the  $\text{Pb}^{2+}$  ions to form highly insoluble  $\text{PbCl}_2$ . Sodium from the water glass replaced the  $\text{Pb}^{2+}$  ions as the stabilizing cation. The acetic acid used in excess as the gelling agent acted as a bidentate group to complex and hold the square pyramidal position above the square planar  $\text{Cu}^{2+}$  site. This apical acetate group is associated with a proton from the highly acidic medium which satisfies the charge neutrality of the compound. This proton occupies an electron-deficient site observed in the electron density map of the structure. The population parameters at this site is 0.5, which is exactly that required for one hydrogen atom per formula unit.

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