Optical and proton magnetic resonance study of copper (II) acetate dimeric molecules in acetonitrile/acetic acid mixtures
by Jennie Li-Ming Wang Dirks

A thesis submitted in partial fulfillment of the requirements for the degree Of MASTER OF SCIENCE in Chemistry
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Abstract:
NMR line width and line shift of the acidic proton of HAc, and the methyl protons of the acetic acid and acetonitrile in CH.COOH/CH CH solutions with and without copper acetate have been 33 measured between -45°C to 37°C with a few measurements at higher temperature. The results, indicate an acid proton exchange between acetic acid monomer and dimer, axial ligand exchange of both acetic acid and acetonitrile on the copper acetate dimeric molecules at all temperatures. In addition, at higher temperatures there is exchange of acetate between acetic acid and the bridging ligands of the copper acetate dimer, with an activation energy of the order of 10 Kcal mol-1

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*Jennie Wang Dirks*

Name

*Dec. 4 1975*

Date

TO

my great husband

OPTICAL AND PROTON MAGNETIC RESONANCE STUDY OF
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JENNIE WANG DIRKS


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# ABSTRACT

NMR line width and line shift of the acidic proton of HAc, and the methyl protons of the acetic acid and acetonitrile in $CH_3COOH/CH_3CH$ solutions with and without copper acetate have been measured between -45°C to 37°C with a few measurements at higher temperature. The results indicate an acid proton exchange between acetic acid monomer and dimer, axial ligand exchange of both acetic acid and acetonitrile on the copper acetate dimeric molecules at all temperatures. In addition, at higher temperatures there is exchange of acetate between acetic acid and the bridging ligands of the copper acetate dimer, with an activation energy of the order of 10 Kcal $mol^{-1}$.

# INTRODUCTION

## Copper Acetate

There are a number of good reviews[1] on the chemistry of copper. Copper(II) acetate is a typical transition metal compound, showing paramagnetism and color due to the presence of partially filled d orbitals. Copper(II) has a $d^9$ configuration. The $t_{2g}^6 e_g^3$ configuration expected for octahedral $d^9$ complexes is subject to a Jahn-Teller distortion. In most Cu(II) complexes this leads four shorter and stronger bonds which are roughly in a plane, and two weaker longer axial bonds. This causes further splitting of the d orbitals as described in Appendix D.

In solution in most organic solvents and in crystalline $Cu_2(CH_3COO)_4 \cdot 2H_2O$ copper acetate exists as a binuclear complex in which the copper (II) ions are bridged by four acetate groups. This dimer has two axial positions available for weaker bonding of solvent or water molecules. The dimer structure is shown in Figure 1. In the crystal the copper (II) ions are 0.22 Å out of the plane of the four acetate oxygen atoms at a distance of 1.97 Å. The distance to the axial ligands is 2.20 Å. One striking feature of this structure is the close approach of the two copper (II) ions, 2.64 Å, which is only slightly greater than the interatomic distance in metallic copper, 2.56 Å. At this distance metal - metal bonding can be strong or weak, and may have multiple character.[2] In this case the interaction is
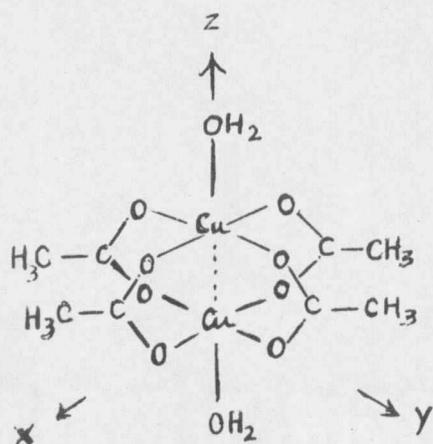
Figure 1.  Schematic expression of the structure of $Cu_2(CH_3COO)_4 \cdot 2H_2O$ molecule

antiferromagnetic as shown by the magnetic susceptibility[3-5] and by

the paramagnetic resonance spectra.[6-13]  There is also evidence on the

nature of the bonding from the uv-visible spectrum, from the crystal

structure,[14,15] and the temperature variation of the magnetic suscep-

tibilities.[16-18]  These are discussed more fully in Appendix D, how-

ever the full explanation of the nature of the copper-copper bond is

still an interesting unsolved problem.[19-20]

Copper acetate exists mainly in the dimeric form in acetic acid

and many other solvents.[21-26]  The dimer spectrum is similar to that of

copper acetate crystals with strong absorbance around 700 nm.  There

have been many attempts to interpret the dimer spectrum,[27-34] which

are considered in more detail in Appendix D.

Our interest in the copper acetate dimer was initially in the

bonding of the axial ligands. NMR spectroscopy is generally useful in

the study of ligand substitution processes,[35-48] and we decided to in-

vestigate the NMR chemical shift and line shape of acetic acid and

acetonitrile protons in the mixed solvent with and without copper

acetate. This solvent system turned out to have unusual and interest-

ing features, since under some conditions small amounts of water pres-

ent will react with the acetonitrile.

## The Reactions Among Acetonitrile, Acetic Acid
### and Water

The reaction of acetonitrile and acetic acid. A number of

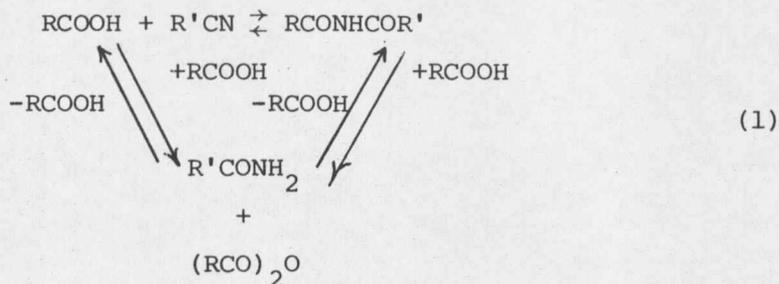peculiarities have been reported in connection with the reaction be-

tween acetonitrile and acetic acid. Kremann, Zoff and Osward[49] re-

ported in 1922, that acetic anhydride and acetamide were present after

refluxing 2 Moles acetic acid with 1 Mole acetonitrile at 98°C for a

few hours. These authors did not examine the reaction mixture chemi-

cally, but based their conclusion on changes in the freezing point.

They also reported that heating an acetamide-acetic anhydride mixture

for 30 hours at 98°C yielded the same equilibrium mixture (83% con-

version to nitrile and acid). On the other hand, however, Davidson

and Skorronek[50] reported that a mixture of 0.10 mole acetonitrile and

0.20 mole of acetic acid gave no test for acetic anhydride after heat-

ing for 48 hours on the steam-bath. In the same paper, however, at a

temperature of about 200°C, Davidson and Skovronek reported that various nitriles and acids reacted at elevated temperature to give not only diamides but also the corresponding anhydride and amide, due to the interlocking equilibria shown below.

$$RCOOH + R'CN \rightleftharpoons RCONHCOR'$$

$$-RCOOH \diagdown \quad \begin{array}{c} +RCOOH \\ -RCOOH \end{array} \quad \diagup +RCOOH$$

$$R'CONH_2$$
$$+$$
$$(RCO)_2O$$

(1)

Moreover, in 1963, equilibria and relative reaction rates in the reactions of acetic and trifluoroacetic acids with acetonitrile and trifluoroacetonitrile were reported by Durrell, Young and Dresdner.[51] In contrast to the results of Davidson and Skovronek, they did not detect the presence of the anhydride-amide pair in any of their four systems. As to the pair of acetic acid-acetonitrile, their end products were still the unchanged acetonitrile and acetic acid. This discrepancy was explained by Durrell et al. as that an excess of free acid was used by Davidson and Skovronek. It can be seen from the diagram (12) that presence of excess acid would force the total equilibrium toward the amide-anhydride pair.

From the previous references and discussion, it is quite reasonable to conclude that at temperatures of lower than 50°C and

without a catalyst the net reaction of our 40%, 30%, 20% and 10%

$HAc/CH_3CN$ is

$$CH_3CN + CH_3COOH \rightleftharpoons CH_3COOH + CH_3CN \qquad (2)$$
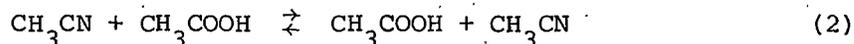
The influence of small amount of water in our acetonitrile/

acetic acid solutions. The IR spectra showed the presence of water,

if the $HAc/CH_3CN$ solutions were prepared less than a week before.

However, after standing for three weeks, there was no more water peak

shown in the IR spectra. Apparently, the presence of HAc accelerates

the hydrolysis of $CH_3CN$.[52] Since there is only a small amount of water

in commercial acetonitrile and acetic acid, by mixing acetic acid and

acetonitrile, we get only a trace of acetamide because the hydrolysis

of acetonitrile.

## RESEARCH OBJECTIVES

Copper acetate dimeric molecule has been an interesting topic in research. Recent literature indicates that with NMR one may study the axial ligand exchange of the dimer. We also believed that there might also be bridging ligand exchange at higher temperature, and wanted to clarify this point by NMR study of an additional mixed solvent system. We were interested in studying copper acetate in acetic acid-acetonitrile solutions to gain further insight into the bonding of axial ligand.

## Dimer/Monomer Equilibrium of Copper(II) Acetate in Mixture of Acetonitrile/Acetic Acid/Water from Optical Measurements

The absorbance due to both copper acetate and water were taken on Cary Model 14 spectrophotometer. Data were taken at different days for 0.005M copper acetate dimer in various percentages of acetic acid/acetonitrile solutions, and the above HAc/CH$_3$CN solutions containing various amounts of water.

The spectrophotometer cell was immersed in a thermostatted water bath of 24.5°C between measurements for some series of measurements. The spectrophotometer cell was equipped with a ball and socket closure and a quartz spacer allowing path lengths of 1, 3, or 10 mm. The water concentrations were calculated from the measured absorbance at 1410 nm in the near infrared using the relationship $M_{H_2O} = 3.9 (a_{1410} - a_{1300})$. It was necessary to add the water concentration in the blank, determined by the same measurement vs. a cell with dilute acetic anhydride in acetonitrile.

Just before or after the near infrared scan the visible spectrum was recorded usually with a 3 mm pathlength, and $a_{690} - a_{490}$ was calculated for a 10 mm pathlength. The dimer has a substantial extinction coefficient at 690 nm ($\varepsilon_{690} - \varepsilon_{490} = 426$) and is responsible for most of the observed blue green color. The monomer absorbs in the same wavelength region, but much less strongly. The value ($\varepsilon_{690} - \varepsilon_{490}) = 35$ is taken from measurement in acetic