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THE ANALYSIS OF STRUCTURE AND STRENGTH OF C-O BOND IN COPPER(II) BENZOATE AND ITS DERIVATIVES BY FTIR SPECTROSCOPY

ZURAIDA KHUSAIMI[1] AND NORBANI ABDULLAH[2]
[1] Chemistry Department, Faculty of Applied Science, Block G, UiTM Section 17, 40200 Shah Alam, Selangor, Malaysia.
[2] Chemistry Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

ABSTRACT

Copper(II) benzoate and its derivatives namely copper(II) 4-flourobenzoate, copper(II) 4-chlorobenzote were prepared by refluxing copper(II) monohydrate with the corresponding acids. The material studied are potential low-dimensional, thermally stable molecular electronics. The structure and strength of respective C-O bond of the ligand of these samples are investigated by Fourier Transform Infrared Spectroscopy (FTIR). Copper(II) 4-flourobenzoate and copper(II) 4-chlorobenzoate are electron-attracting substituents and have lower C-O bond strength than copper(II) benzoate, and thus stronger bridging bond between the ligand and the copper(II) ion. The order of the strength of the bridging bond is as follows:

Copper(II) benzoate ↓ *Strength increases*
Copper(II) 4-chlorobenzoate
Copper(II) 4-flourobenzote

Keyword: *Low dimensional molecular electronics, Copper(II) benzoate, C-O bond, FTIR.*

INTRODUCTION

Reliability and energy saving nature of electronics are highly improved by miniaturization (1). This opens a new dimension of electronics performed by molecules. Many organic conductors are low-dimensional, having a planar structure and are arranged in linear columns. Metals are conductors due to the presence of mobile electrons. It transports electrical charge through solid. In organic solids, the electrons are strongly involved in bonding, thus majority of organic solids are electrical insulators. However, due to conjugation of electrons, organic compounds can also be conductors.

Low dimensional molecular electronics are mostly anisotropic, in which electrons move in linear arrangements parallel to the columnar axis. Some of the vastly examined and promising materials for usage in organic electrical devices are charge-transfer complexes and conjugated polymers.

In FTIR, molecules absorb certain frequencies and convert it into energy of molecular vibration, which can be further divided into bending and stretching. The molecular vibration is determined by the bond strength (or stiffness) and the masses of the atoms. However, not all molecules are infrared active. There has to be a change in dipole moment or polarity resulting from the vibrations for a molecule to be observed in infrared (2,3).

Interpretation of Spectra

Changes in molecular environment may cause shifts in absorption position and changes in band contours. The absence of absorption in the assigned ranges for particular functional groups can be used as evidence for the absence of such group. This must be used cautiously since certain structural characteristics may cause a broad band and go unnoticed or the absence could be due to infrared inactive.
Some of the more common functional groups are listed in Table 1.

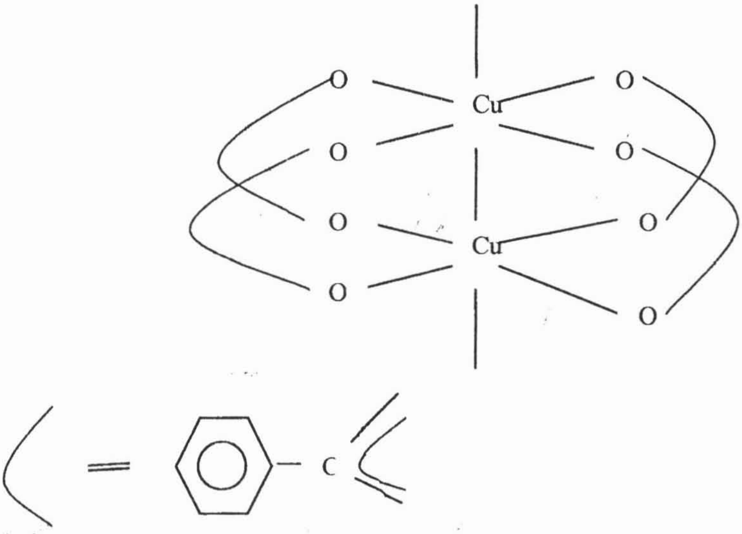
Structure and Bonding of Copper(II) Benzoate and its Derivatives

Copper(II) benzoate (CB) is an example of coordination compound. Its structure is yet to be published. The proposed structure (Figure 1) is based on the published structure of copper(II) acetate (4). The empirical formula of CB is $Cu(C_6H_5COO)_2$

Functional Group	Wavenumber (cm^{-1})
C-H Aromatic	3100-3000 (m) 1630-1440 (s)
-COO Asymmetrical stretching	1650-1550 (s)
-COO Symmetrical stretching	1420-1300 (w)
Monosubstituted aromatic ring C – C ring stretch	1600-1500 (m)
Monosubstituted aromatic ring - C-H (out of plane) bend	750 ± 25 (s) 695 ± 15 (s)

s, strong; m, medium; w, weak

Table 1. FTIR data of selected functional groups and bonds



Key :

Figure1 Proposed structure of copper (II) benzoate

The proposed structure shows a dimer made up of two square-planar copper(II) ions bonded to four bridging bidentate benzoato ligands. There may be weak Cu-Cu bond within the dimer. It is postulated that the dimer may oligomerise or polymerise to form longer chains due to the presence of unpaired d electron in each copper(II) ion.

Copper(II) ion is a d^9 system. The sp^3d^2 hybridisation with initial octahedral structure reduces to square planar made up of four short Cu-ligand bonds and two longer trans bonds as a result of Jahn-Teller (4) or orthogonal effect

The benzoato ligand has symmetrical bidentate coordination and bridging to two different copper(II) ions. Its aromatic ring provides a resonance structure which may result in conjugation to the bridging bond by the overlapping of π orbitals.

Electron attracting substituent, such as F, and Cl, will affect the aromaticity of the ring, which will then affect the electron conjugation with the bridging bonds. The effect may be due to inductive and/or mesomeric effects. The inductive effect acts through sigma (σ) electrons or bonds, while the mesomeric effect acts through π electrons or bonds (5).

The halogens have negative inductive effect because they attract the aromatic electrons out of the ring (Figure 2). This effect is proportional to the electronegativity of the atom, the expected order is F > Cl (6).

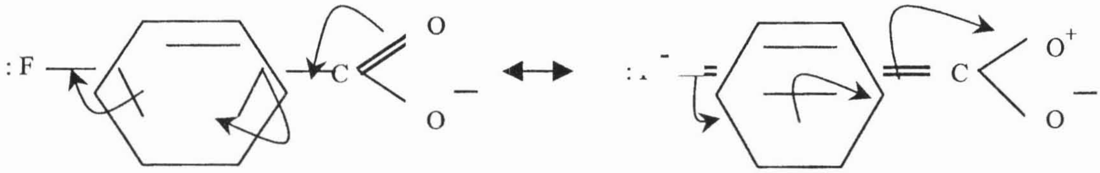


Figure 2. The negative inductive effect of F, on benzoato ligand

The mesomeric effect arises when the substituent has unshared electron pairs or multiple bonds, which can be delocalised into the ring (Figure 3). This effect is affected by the size of the substituent; small size favours electron-donating effect while larger size disfavour it.

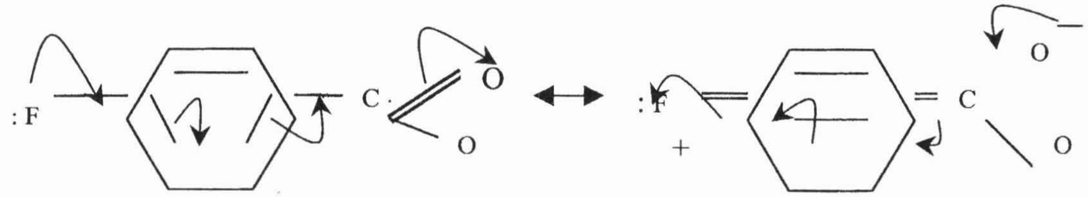


Figure 3. The mesomeric effect of F on benzoato ligand

Thus the smaller fluorine is expected to exert strong mesomeric and strong negative inductive effects, while the bigger chlorine will exert weak mesomeric and weak negative inductive effects.

MATERIALS AND METHODS

Copper(II) benzoate, copper(II) 4-flourobenzote and copper(II) 4-chlorobenzoate were prepared by the following method.

Copper(II) benzoate

A suspension of copper(II) acetate monohydrate and benzoic acid mixed in a molar ratio of 1:2 were refluxed for 24 hours in acetonitrile in a round-bottomed flask connected to a reflux condenser. The mixture was constantly stirred using a magnetic stirring bar. The reaction mixture was left to cool to room temperature and the powder obtained was filtered, rinsed with ethanol and dried in an oven at 60°C for 30 minutes. The powder was purified by heating with ethanol for 30 minutes. The solid residue was filtered, washed with ethanol and dried in the oven at 60 °C for 30 minutes.

Copper(II) 4-Fluorobenzoate, Copper(II) 4-Chlorobenzoate

Copper(II) 4-fluorobenzoate, copper(II) 4-chlorobenzoate, were similarly prepared from copper(II) acetate monohydrate and 4-flourobenzoic acid and 4-chlorobenzoic acid, respectively.

The instrument for Fourier Transform Infrared analyses were Perkin Elmer model Spectrum 2000.

Mull in Nujol

10-20 mg of solid sample was ground in a smooth agate mortar with a pestle into a fine powder. One drop of Nujol (paraffin) was added and the mixture continually grounded until the solid is completely suspended in oil. The paste was then rubbed to a salt plate using the pestle, and a second plate was pressed on to the paste. The two plates were moved against each other until the paste is completely and evenly spread and no unfilled space can be seen.

RESULTS AND DISCUSSION

Copper(II) 4-fluorobenzoate and copper(II) 4-chlorobenzoate were derivatives of CB studied. Each derivative contains an electron-attracting substituent at the *para*-position.
The FTIR spectra of CB and CB derivatives in Nujol are shown in Figure 4, 5 and 6.
The data for bidentate bridging –COO asymmetrical stretch are listed in Table 2.

Materials in KBr	**Bands in Nujol (cm^{-1})**
Copper(II) benzoate	1612
Copper (II) 4-fluorobenzoate	1548
Copper (II) 4-chlorobenzoate	1563

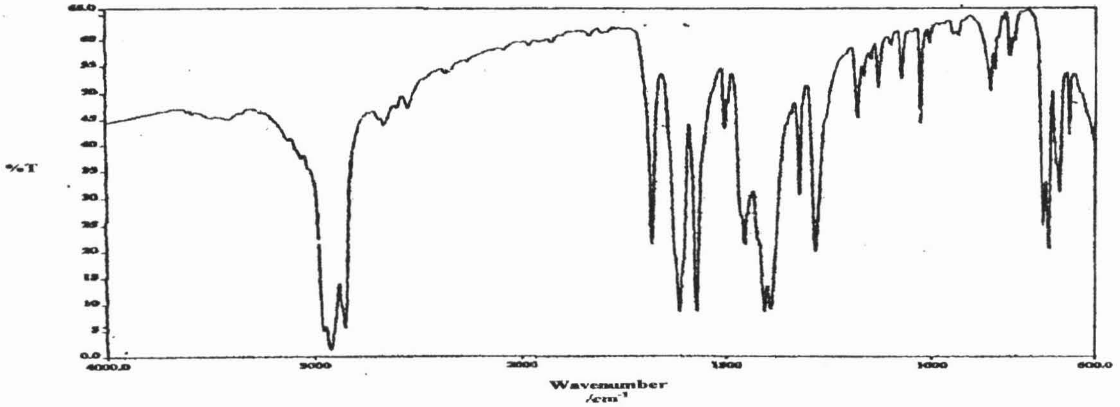
Table 2. FTIR data for bidentate bridging –COO asymmetrical stretch in copper(II) benzoate and its derivatives

The results show that the wavenumber of bridging bidentate C-O asymmetrical stretch for all the derivatives are lower than that for CB. The reduced C-O bond order in the derivatives may mean that C-O bonds are weaker in the electron-poor ligands. This may cause an increase bond multiplicity and electron delocalisation in the derivatives as a result of increase pπ-dπ orbital overlaps due to back donation from the electron-rich copper(II) ion, producing stronger bridging bonds between the ligands and the central copper(II) ions.

The order of bridging C-O bond strength is benzoato > 4-chlorobenzoato > 4-fluorobenzoato.

The order chloro < fluoro follows the order of increasing electronegativity or decreasing size of the substituents. It seems that the less electronegative Cl substituent reduced the bridging C-O bond strength the least, or the most electronegative substituent weaken the bond most. Thus the main factor affecting the bridging C-O bond strength seems to be the negative inductive effect, and not the mesomeric effect.

Figure 4. FTIR spectrum of copper(II) benzoate in Nujol



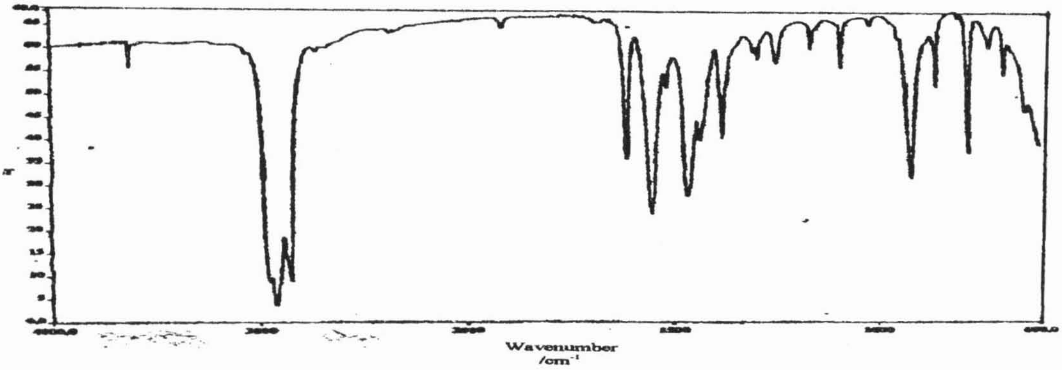


Figure 5. FTIR spectrum of copper(II) 4-flourobenzoate in Nujol

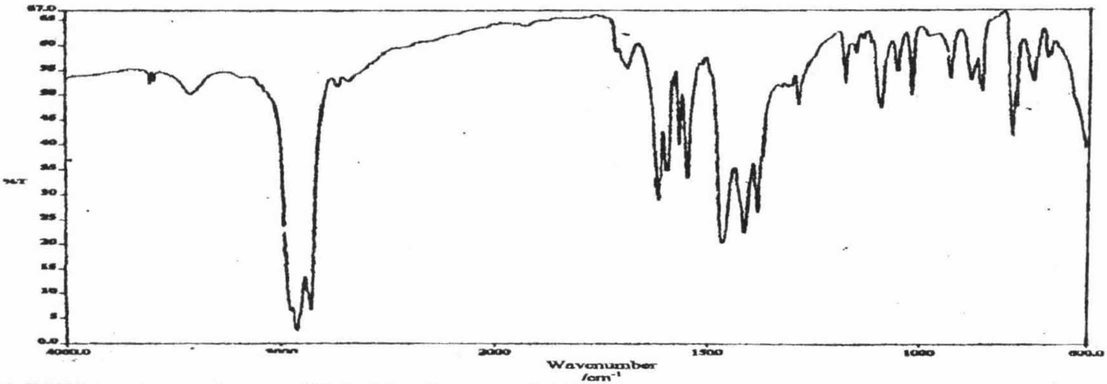


Figure 6. FTIR spectrum of copper(II) 4-chlorobenzoate in Nujol

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