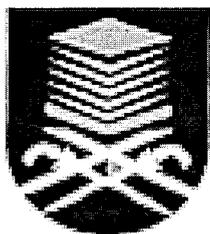


**SYNTHESIS AND FOURIER TRANSFORM INFRARED  
SPECTROSCOPIC STUDIES OF C-O BOND IN THE  
NICKEL(II) BENZOATE DERIVATIVES SUBSTITUED WITH  
ELECTRON-ATTRACTING GROUPS**



**BUREAU OF RESEARCH AND CONSULTANCY  
UNIVERSITY TEKNOLOGI MARA  
40450 SHAH ALAM, SELANGOR  
MALAYSIA**

**BY**

**PUAN ZURAIDA KHUSAIMI  
PUAN AZLIN SANUSI**

**SEPTEMBER 2003**

# CONTENTS

Report Submission Letter	i
Research Members	ii
Acknowledgement	iii
Contents	1
CHAPTER 1 INTRODUCTION	3
CHAPTER 2 LITERATURE REVIEW	4
2.1 Metallomesogens	4
2.1.1 Dithene complexes of nickel, palladium and platinum	4
2.1.2 $\beta$ -diketonato complex type	6
2.1.2.1 Copper complexes with eight peripheral chains	6
2.1.2.2 Octahedral iron complexes	8
2.1.3 Dinuclear carboxylate complex	8
2.1.3.1 Copper carboxylates	9
2.2 Application as Molecular Electronics	11
2.2.1 (BEDT-TTF) <sub>3</sub> CuCl <sub>4</sub> .H <sub>2</sub> O	12
2.2.2 TCNQ-TTF	13
2.2.3 Conjugated polymers	16
2.3 An example of synthesis of polymers containing conjugated –C=C- bonds to produce electrically conductive polymer	18
2.4 Structure and Bonding of Nickel(II) benzoate and its derivatives	21
2.4.1 Ligand field theory and octahedral complexes	21
2.4.2 Bonding in Nickel(II) Benzoate	23
2.5 Interpretation of spectra	24
CHAPTER 3 EXPERIMENTAL WORK	25
3.1 Objectives of Experiments	25
3.2 Preparation of Materials	25
3.2.1 Nickel(II) 4-fluorbenzoate	25
3.2.2 Nickel(II) 4-chlorobenzoate, nickel(II) 4-bromobenzoate and nickel(II) 4-iodobenzoate	25
3.3 Analyses	26

CHAPTER 4 RESULTS AND DISCUSSION	27
4.1 Nickel(II) 4-fluorbenzoate, Synthesis and structure	27
4.2 Other derivatives of Nickel(II) Benzoate	28
CHAPTER 5 CONCLUSION AND SUGGESTIONS FOR FUTURE WORK	30
5.1 Conclusion	30
5.2 Suggestions for Future Work	30
REFERENCES	31
APPENDIX	34

## CHAPTER 1: INTRODUCTION

Miniaturization of electronic devices increases the reliability and energy saving nature of electronic devices [8]. For the last 10 years or so scientists like Tour and Reed [5] has been enthusiastically studying, synthesizing and isolating molecules exhibiting conductive, semi-conductive and super-conductive ability. One of the major advantage in the manufacturing of molecular electronics is that they are self-assembled, by simply putting the right ingredients into a beaker, unlike time consuming microchip-producing technique. Computing speed can also be revolutionized to millions of times faster than of silicon material [5].

Nickel(II) benzoate is a metallomesogens, a potential low-dimensional electronic material. Its structure is assumed to follow the ligand-field theory [12].

The current research has three main objectives, namely to:

- 1) Synthesize the derivatives of nickel(II) benzoate, i.e. nickel(II) 4-fluorobenzoate, nickel(II) 4-chlorobenzoate, nickel(II) 4-bromobenzoate and nickel(II) 4-iodobenzoate.
- 2) Study the effect of electron-attracting substituents attached at the para-position of the benzoato ligand, namely, fluoro, chloro, bromo and iodo, on the strength of the bridging ligand.

The analysis will focus on the wavenumber of C-O bond of the benzoato ligand, which is inversely related to the strength of the bridging bond.

The sample was prepared by reflux method and the product was analysed using Spectrum 2000 Fourier Transform Infrared Spectrometer.

Copper(II) benzoate, a coordination compound has been studied (7), and shown to have electronic properties and thermal stability. It was thought that nickel(II) benzoate, another coordination compound might contain similar properties and is a potential molecular electronics.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Metallomesogens and Examples of Metallomesogens

Metallomesogens are metal-containing liquid crystals. Liquid crystals have been known for the last hundred years [1]. It has definite ordered structure (mesomorphic state). Usually composed of flat planar molecules with high degree of symmetry and its properties are electrically affected.

Metallomesogen is a relatively new compound (found in the last twenty years or so [1]). Upon synthesis and characterization it was found to carry properties like colour, magnetism, polarizability and multiple localized charges. Most of its shapes are square planar, octahedral, square pyramidal and lantern structure (rod-like, disc-like structure.). The optical property of metallomesogens are found to show strong birefringence, dichroism and nonlinear optical behaviour. It is paramagnetic and has various orientation in magnetic field. Metallomesogens also show electro-optical properties i.e. a ferroelectric behaviour [2,3].

The most interesting property for a metallomesogens is it can act as low-dimensional conductors. This potential application of metallomesogens in material science is associated with the possibility of electronic communication between metal atoms through  $\pi$  systems of bridging ligands [4].

Follows are some examples of metallomesogens.

#### 2.1.1 Dithene complexes of nickel, palladium and platinum [2]

In general, dithiolato complexes are square planar, and one can imagine a planar terphenyl like structure for complexes of that type (Fig. 2.1). So, first in Grenoble and mostly in Mueller-Westerhoff's laboratory at IBM in San Jose (California), dithene complexes of nickel, platinum and palladium were synthesized and their mesomorphic properties investigated.