CHAPTER 4
RESULTS AND DISCUSSION

4.1 Thermogravimetry

The thermograms of copper(II) benzoate (CB), copper(II) 4-fluorobenzoate (CFB), copper(II) 4-chlorobenzoate (CCB), copper(II) 4-bromobenzoate (CBB), copper(II) 4-iodobenzoate (CIB), copper(II) pentafluorobenzoate (CPFB), copper(II) 4-nitrobenzoate (CNB), and copper(II) 3,5-dinitrobenzoate (CDNB) are shown in Figure 4.1 – 4.8, and the data collected in Table 4.1.

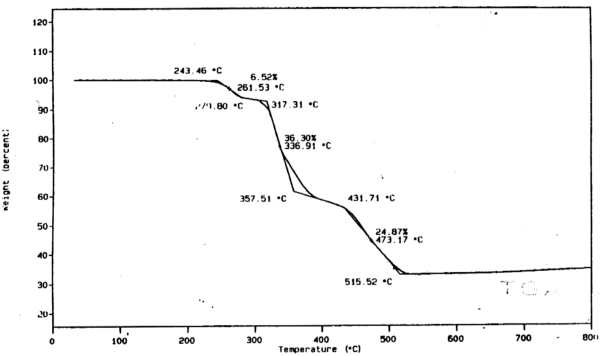


Figure 4.1 Thermogram of copper(II) benzoate

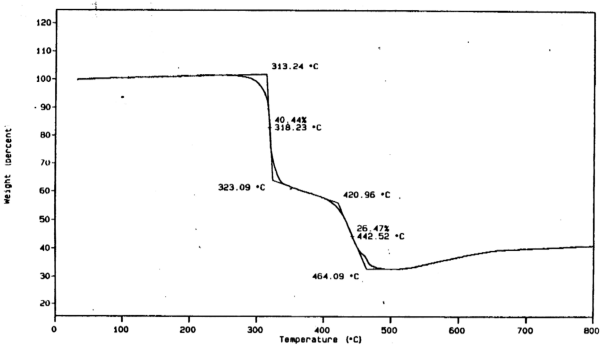


Figure 4.2 Thermogram of copper(II) 4-fluorobenzoate

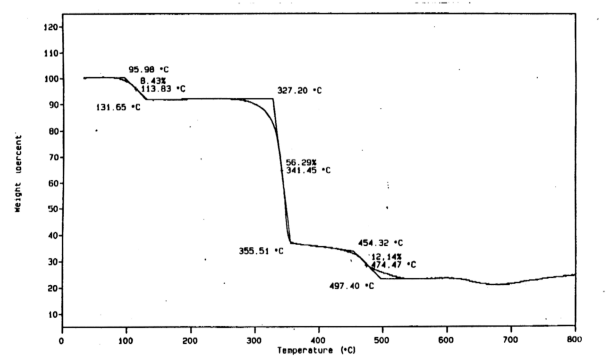


Figure 4.3 Thermogram of copper(II) 4-chlorobenzoate

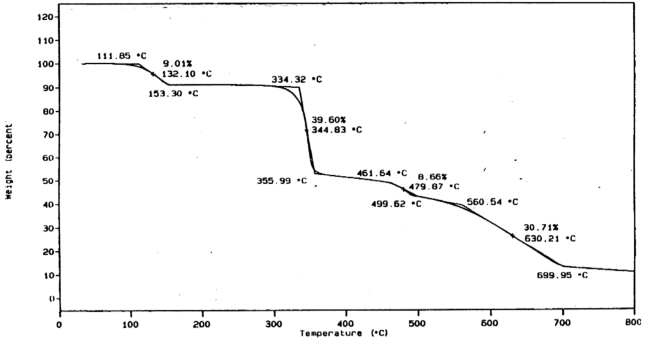


Figure 4.4 Thermogram of copper(II) 4-bromobenzoate

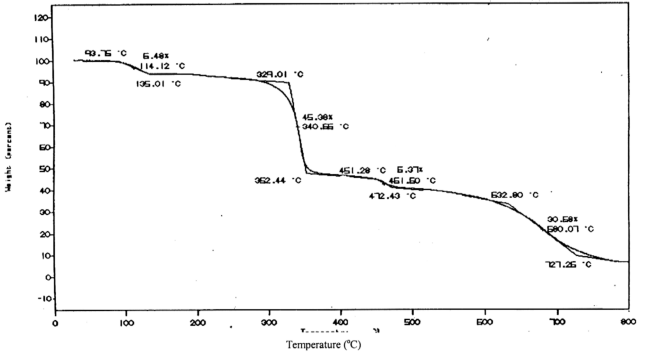


Figure 4.5 Thermogram of copper(II) 4-iodobenzoate

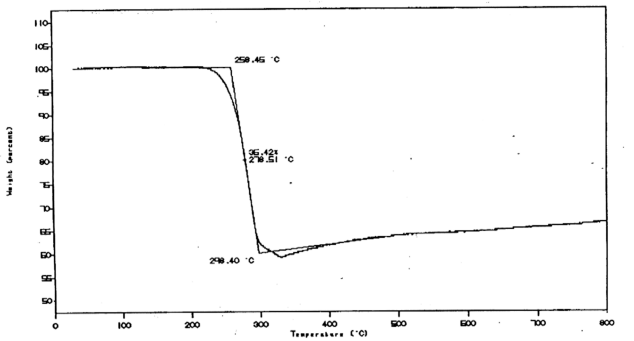


Figure 4.6 Thermogram of copper(II) pentafluorobenzoate

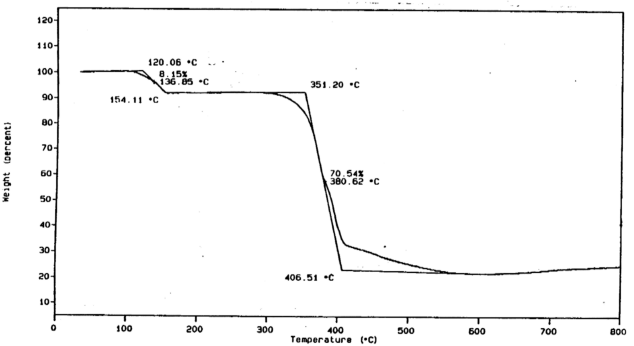


Figure 4.7 Thermogram of copper(II) 4-nitrobenzoate

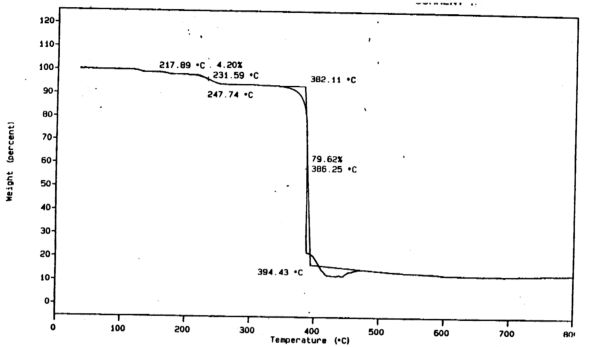


Figure 4.8 Thermogram of copper(II) 3,5-dinitrobenzoate

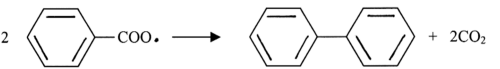
Table 4.1 TGA data of copper(II) benzoate and substituents.

Materials	Mass (mg)	Initial Decomposition Temperature T_d (°C)	Weight loss (%)	Final Decomposition Temperature T_d (°C)	Residue (%)
Copper(II) benzoate (CB)	3.617	243.5	67.7	515	32.3
Copper(II) 4-fluorobenzoate (CFB)	1.480	313	66.9	464	33.1
Copper(II) 4-chlorobenzoate (CCB)	1.076	327	68.4	497	31.6
Copper(II) 4-bromobenzoate (CBB)	3.059	334	79.0	699	21.0
Copper(II) 4-iodobenzoate (CIB)	3.133	329	82.4	727	17.6
Copper(II) pentafluoroben zoate (CPFB)	1.454	258	36.4	293	63.6
Copper(II) 4-nitrobenzoate (CNB)	1.157	351	70.5	406	29.5
Copper(II) 3,5-dinitrobenzoate (CDNB)	1.813	382	79.6	394	20.4

The thermograms of CB and its derivatives show that the decomposition temperature ranges from 243.5°C to 382°C, with CB the least thermally stable and CDNB the most thermally stable. The order of thermal stability is:

CDNB > CNB > CBB > CCB > CIB > CFB > CPFB > CB

The thermogram of CB (Figure 4.1) shows that there was gradual decomposition from 243.5 °C to 515.0 °C, with total weight loss of 67.7 % and leaving 32.3 % residue above this temperature. The decomposition of CB is postulated to begin with breaking of the bridging coordinate bond between the benzoato ligand and copper(II) ion to produce benzoyloxy radical. The radical then decomposed to volatiles such as carbon dioxide and biphenyl, as shown below. The residue from the decomposition of CB may be copper(II) oxide or other copper(II) compounds.



benzoyloxy radical biphenyl

It is noted that all the CB derivatives containing electron-attracting substituents are thermally more stable than CB. The higher thermal stability may be due to resonance stabilisation effect which increases the electron density at the bridging bond between the ligand and the central copper(II) ion, thus strengthening it. As an example, the resonance stabilisation of 4-fluorobenzoato ligand is shown in Figure 4.10.

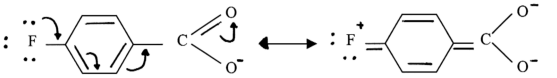


Figure 4.10 Resonance stabilisation of 4-fluorobenzoato ligand

The order of thermal stability of monohalogenated derivatives, that is Br > Cl > I > F, needs further explanation. For fluoro-, chloro-, and bromo- derivatives, the order of thermal stability is in good agreement with the order of electronegativity of the atoms: the higher the electronegativity the lower the thermal stability. It is reasonable that the more electronegative fluorin atom will decrease resonance stabilisation when compared to the less eletronegative bromine atom.

For iodo derivative, the thermal stability is not as expected if based on the order of electronegativity of the atom, but is to be expected if based on the size of the atom. Iodine, being the biggest of the halogen, would reduce the overlap between the p orbitals of iodine and aromatic carbon because of the longer carbon-iodine sigma (σ) bond, which reduces resonance stabilisation of the ligand.

The arguments above is supported by the thermal stability of CPFB when compared to the monohalogenated derivatives. The five fluorin atoms at the ring resulted in the lowest resonance stabilisation of the material, thus making it the least stable of all the halogenated derivatives.

It is also noted that both nitro derivatives are thermally more stable than the halogenated derivatives. The decomposition temperatures of CNB and CDNB are 351 °C and 382 °C respectively. It is observed that through resonance stabilisation of the nitro-ligands (Figure 4.11), the materials are polar and this may increase the thermal stability. Thus the higher thermal stability of the dinitro derivative is explained.

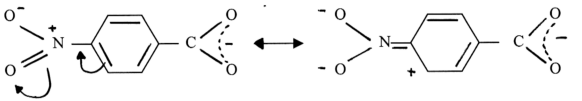


Figure 4.11 Resonance stabilisation of 4-nitrobenzoato ligand

4.2 Differential Scanning Calorimetry

The differential scanning chromatograms (DSC) of copper(II) benzoate and its derivatives are shown in Figure 4.12 – 4.19, and the data collected in Table 4.2.

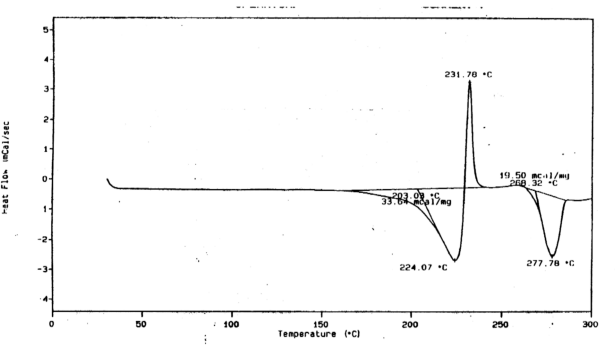


Figure 4.12 DSC curve of copper(II) benzoate

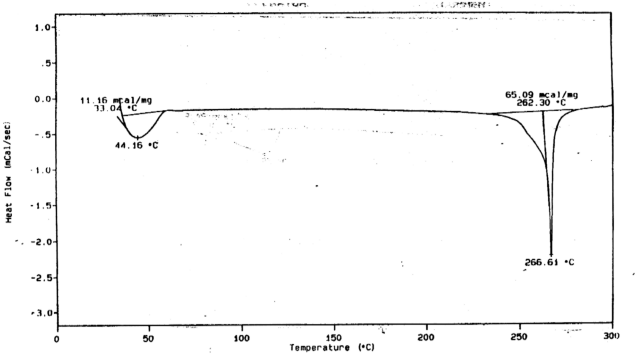


Figure 4.13 DSC curve of copper(II) 4-fluorobenzoate

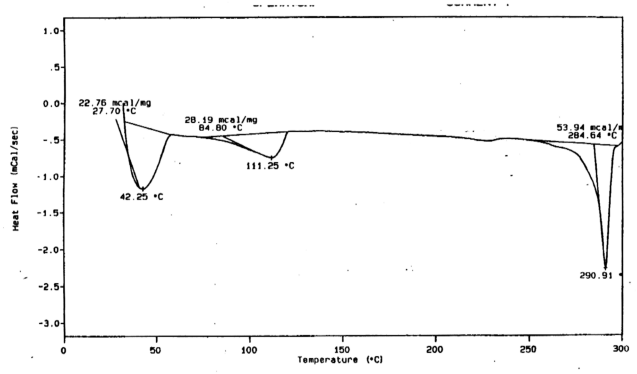


Figure 4.14 DSC curve of copper(II) 4-chlorobenzoate

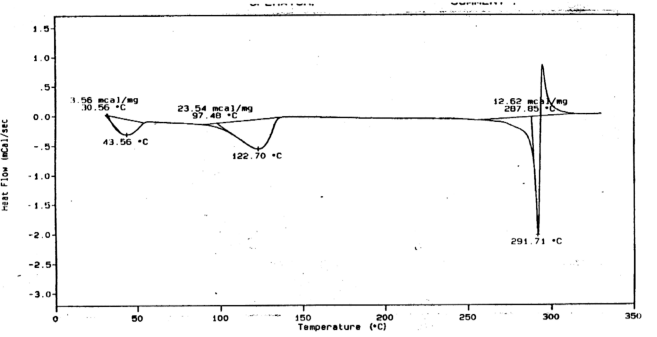


Figure 4.15 DSC curve of copper(II) 4-bromobenzoate

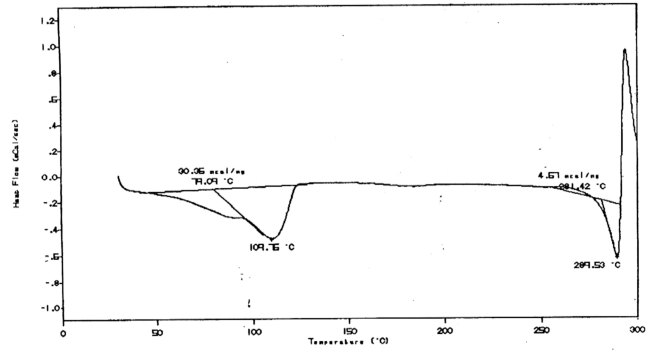


Figure 4.16 DSC curve of copper(II) 4-iodobenzoate

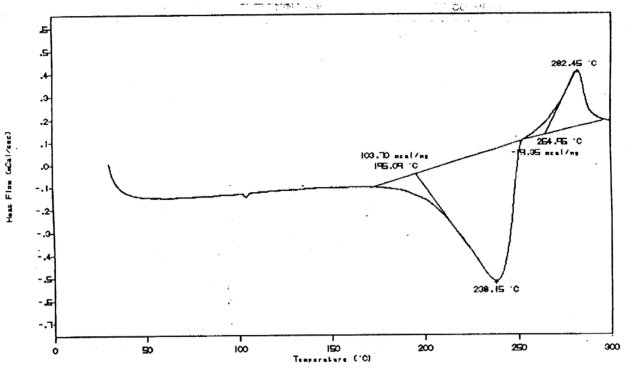


Figure 4.17 DSC curve of copper(II) pentafluorobenzoate

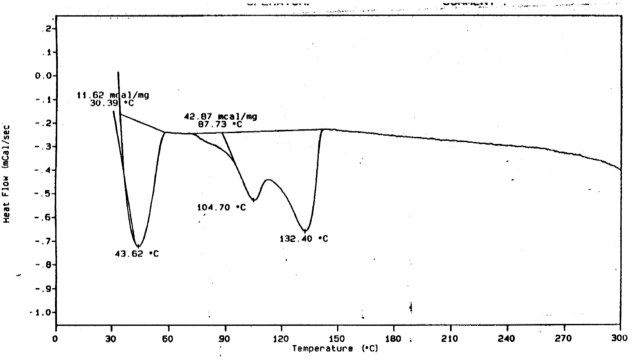


Figure 4.18 DSC curve of copper(II) 4-nitrobenzoate

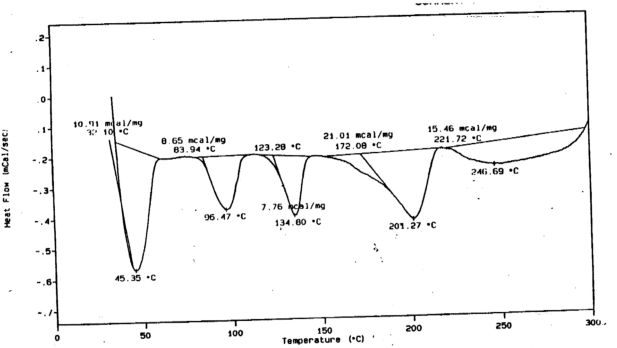


Figure 4.19 DSC curve of copper(II) 3,5-dinitrobenzoate

Table 4.2 DSC data of the copper(II) benzoate and substituents

Materials	T_1 (°C)	ΔH_1 (mcal/mg)	T_2 (°C)	ΔH_2 (mcal/mg)	T_3 (°C)	ΔH_3 (mcal/mg)
Copper(II) benzoate (CB)	224	+33.6	232	Negative	278	+268
Copper(II) 4-fluorobenzoate (CFB)	-	-	267	+65		
Copper(II) 4-chlorobenzoate (CCB)	111	+28	290	+54		
Copper(II) 4-bromobenzoate (CBB)	122	+24	292	+13		
Copper(II) 4-iodobenzoate (CIB)	109	+30	290	+4.7		
Copper(II) pentafluoroben zoate (CPFB)	238	+10.4	282	-9.4		
Copper(II) 4-nitrobenzoate (CNB)	105	+43				
Copper(II) 3,5-dinitrobenzoate (CDNB)	96	+8.7	134	+7.8	201	+15

The DSC of copper(II) benzoate, CB (Figure 4.12) shows two endotherms at 224°C and 278°C separated by an exotherm at 232°C. The first endotherm occur at temperature lower than the decomposition temperature of CB at 244 °C. It is associated with the energy needed to break the bridging bond between the benzoato ligand and copper(II) ion, as suggested in Section 4.1. The exotherm at 231°C may results from the heat evolved when volatiles from the decomposition of the benzoyloxy radical were formed. The final endotherm at 278°C may be due to the breaking of Cu-Cu bonds before the material decomposed completely.

The DSC of all the derivatives show similar trends as for CB and may be similarly explained. For monohalogenated derivatives, the first endotherm associated with the energy needed to break the bridging bonds occur at higher temperature compared to CB, and are due to the stronger bonds, as suggested in Section 4.1. The exotherm and final endotherm are not observable in these materials at temperature lower than 300°C but may be observed at higher temperatures, consistent with the materials being more thermally stable than CB.

In support for the above explanation, DSC of copper(II) pentafluorobenzoate (CPFB) showed an endotherm at 238°C and an exotherm at 282°C, which occur at higher temperatures than for CB but at lower temperatures than the monohalogenated derivatives, in agreement with the order of its thermal stability. The final endotherm of CPFB is not observable below 300°C but is expected to be observable at higher temperature.

DSC of copper(II) 4-nitrobenzoate (CNB) and copper(II) 3,5-dinitrobenzoate show many small endotherms that may be due to some internal rearrangements of the molecules and removal of coordinated solvent molecules. The endotherms and exotherms that correspond to the breaking of the bridging bonds, formation of volatiles and the breaking of the copper-copper bonds, as suggested for CB, are not observable in these materials at temperatures lower than 300°C but may be observable at higher temperature, in agreement with their higher thermal stability.

References

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