

CHAPTER 6

THERMAL ANALYSIS AND MASS SPECTROMETRY

6.1 INTRODUCTION

Thermal analysis in its most general terms can be defined as a group of techniques in which a physical change of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature change [1].

All the complexes that were synthesized underwent two specific types of thermal analysis, Thermogravimetry (TG) measurements and Differential Scanning Calorimetry (DSC) measurements. TG simply measures the amount of weight lost by the sample over a controlled temperature range, while DSC is concerned with the energy changes occurring in the sample, i.e. whether the reaction in question is endothermic or exothermic ($\Delta H > 0$) [1].

It is important to note that when using TG as a means of analysis, there are potentially a number of sources of error which one must be aware of. These include measurement of weight by the balance, random fluctuations of the balance mechanism and reaction between sample and container or atmosphere, to name but a few. Most of the sources of error can be corrected while others are interrelated and cannot be assessed separately [1].

DSC is also open to various sources of error. These are normally related to the sample and to the instrument itself. Sample factors include, amount of sample, particle size and sample packing, while experimental factors include, heating rate, sample holder materials and atmosphere surrounding sample [1].

DSC focuses on the energy changes that take place, peaks such as the exothermic and endothermic peaks, as well as peaks associated with other types of thermal events are of importance. Glass transition is an indication that the structure has undergone a transition from a rigid to a flexible structure. Crystallisation is a peak which indicates that further crystallisation or recrystallisation has occurred within the complex due to the heating of the sample. This is observed as an exotherm preceding the melting endotherm [1].

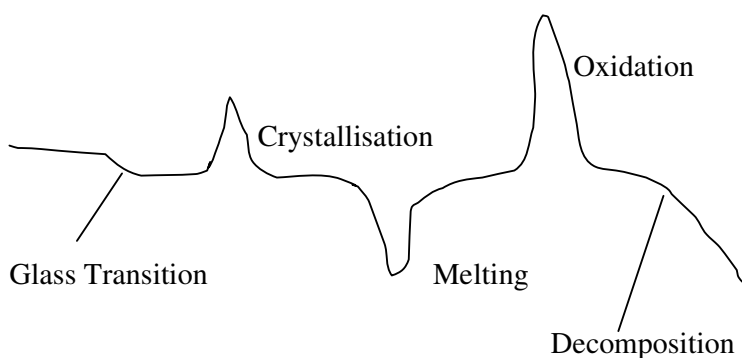


Fig. 6.1 [1] Important DSC peaks

It was hoped that, due to the variety of the type of substituents in the benzoate anion, it may be possible to distinguish thermal events as a function of the electronic properties or size of the substituent group. This study would also make it possible to get an indication of the relative energy of dissociation or decomposition of the different groups in the complex. Should these complexes crystallise in more than one crystal system and/or space group, it could be expected that a variety of different enthalpy values for say the release of thiourea could be expected.

6.2 APPLICATIONS OF THERMOGRAVIMETRY (TG) [2]

As a matter of interest, TG has many applications other than for the analysis used in this project. These include:

- Thermal Stability
- Kinetic Studies
- Material Characterisation
- Corrosion Studies
- Simulation of industrial processes
- Compositional Analysis

6.3 EXPERIMENTAL

TG – DSC analysis was carried out on the STA 409 EP NETZCH and TA control system NETZCH with an acquisition rate of 1.5 points/K and a heating rate of 5 K/min in platinum crucibles which were open to air, as some test runs at heating rates of 1, 2, 3, 5 K/min yielded identical results. All complexes were heated to a temperature of 1200 °C, to ensure complete decomposition of the complexes.

The TG % mass loss ranges and the actual mass losses were obtained using the standard thermal software. It is known that the software supplied with the equipment has some minor inaccuracies, reflected by the fact that some samples gave a mass loss of more than 100 %. Apart from instrumentation and software problems, the fact that gas flow control during the experiment was done by controlling the valve on the gas bottle could have resulted in some variations in measurements. The presence of water was ruled out as no corresponding peak in the TG was observed at temperatures around 100°C. It should also be noted that the sample which gave one of the highest total mass losses (over 100%) was the 2-fluoro complex which has a known crystal structure described in chapter 2, therefore the inaccuracies are not related to the sample.

6.4 DISCUSSION OF THE RESULTS OF THE THERMAL STUDIES OF THE COMPLEXES

6.4.1 ENDOTHERMIC AND EXOTHERMIC TRANSITIONS

These are the most important transitions recorded by DSC techniques. Typical endothermic effects include melting, boiling and evaporation which require energy to break solid state forces. Exothermic effects include freezing as it involves the release of thermal energy as the sample crystallises from the melt [3]. In terms of the analysis at hand, the melting of the complex is of importance.

6.5 TRENDS IN THERMAL RESULTS

The thermal decomposition of all the complexes is a multi-stage process. The endothermic and exothermic peaks that are seen in the DSC spectra, for the most part, occur at the same temperatures with corresponding mass loss in the TG spectra. Those peaks in the DSC spectrum which are not accompanied by a corresponding peak in the TG spectrum normally, indicate a phase change [4].

Overall the thermographs of all the complexes are relatively similar as is expected due to the similarities in the nature of the complexes. However, important differences and trends are visible when analysed closely.

6.5.1 DSC

In terms of the DSC results all the complexes except the 2-chloro, 2-methyl and 4-methoxy complexes have endothermic peaks relating to their respective melting points. The majority of the complexes show a general trend of having seven distinct endothermic and exothermic peaks. Their relation to the % mass loss are discussed later.

In the temperature region of approximately 340°C – 800°C all the complexes are very similar, showing two exothermic peaks at approximately 350°C (no mass loss) and 400°C (mass loss) respectively and two endothermic peaks at approximately 630°C and 800°C. The differences in the complexes are between room temperature and just over 200°C.

Firstly the only four complexes which produced diffraction quality single crystals that were shown to be isostructural (see Chapter 2) plus the 3-bromo complex, show one large endothermic peak at 200°C + which coincides with their melting points. All of the remaining complexes have three peaks in the region at approximately 150°C , 170°C and 200°C. In all cases the peaks at 170°C and 200°C are endothermic peaks while the peak at 150°C is an endothermic peak in most cases but in the 3-nitro, 3-methyl, 3-chloro and 2-hydroxy it is an exothermic peak. The peaks at 150°C and 200°C relate to the thiourea molecules while the peak at 170°C relates to the melting points. The fact that the thiourea molecules come off at different temperatures can be compared with the three water loss steps from hydrated copper

sulphate where by two water molecules are lost at 65°C, two more at 90°C and the final molecule at 220°C [5].

6.5.2 ENTHALPY VALUES OF THE COMPLEXES

COMPLEX	ENTHALPY (kJ/mol) IN THE REGION RT-200°C
Tl-3-fluorobenzoate-thiourea	437 *
Tl-2-fluorobenzoate-thiourea	536 *
Tl-3-aminobenzoate-thiourea	419 *
Tl-benzoate-thiourea	492 *
Tl-3-bromobenzoate-thiourea	487
Tl-2-methylbenzoate-thiourea	420
<hr/>	
Tl-2-aminobenzoate-thiourea	286
Tl-4-aminobenzoate-thiourea	356
Tl-2-nitrobenzoate-thiourea	Not available
Tl-3-nitrobenzoate-thiourea	Not available
Tl-4-nitrobenzoate-thiourea	118
Tl-4-fluorobenzoate-thiourea	305
Tl-2-bromobenzoate-thiourea	244
Tl-4-bromobenzoate-thiourea	288
Tl-2-chlorobenzoate-thiourea	319
Tl-3-chlorobenzoate-thiourea	295
Tl-4-chlorobenzoate-thiourea	313
Tl-3-methylbenzoate-thiourea	233
Tl-4-methylbenzoate-thiourea	270
Tl-2-hydroxybenzoate-thiourea	267
Tl-4-methoxybenzoate-thiourea	147

Note * denotes single crystal structure obtained

Table 6.1 Enthalpy values for all the complexes.

The enthalpy values were determined from the experimental measurements obtained for thermal events occurring at up to 200°C. This was proven by accurate mass spectroscopy to be associated with the loss of all four thiourea molecules. A standard calibration curve to convert KJ/g to KJ/mole was used.

Table 6.1 above shows that in terms of enthalpy values the complexes fall into two distinct groups, in one group, the four single crystal structures (*) plus the 3-bromo and 2-methyl complexes and in the other group, the remaining complexes. Except for the 2-methyl complex, the higher enthalpy values of the first group can be linked or attributed to the large single endothermic peak at around 200°C which is indicative of the four single crystal structures and the 3-bromo complex (see 6.5.1). No clear reason could be ascribed for the relatively high value registered for the 2-methyl complex.

6.5.3 TG

Like the DSC results, the TG results are very similar for all the complexes with a general pattern or trend visible throughout.

By running a thermograph of the 4-amino complex without thiourea it is clear that the endothermic peaks between RT - 200°C relate to the thiourea mass loss as all the other peaks are identical to the complexes. The single crystal x-ray structure for this compound has been determined (see chapter 2). This result is also substantiated by mass spectroscopy studies in this temperature range, clearly indicating the loss of thiourea.

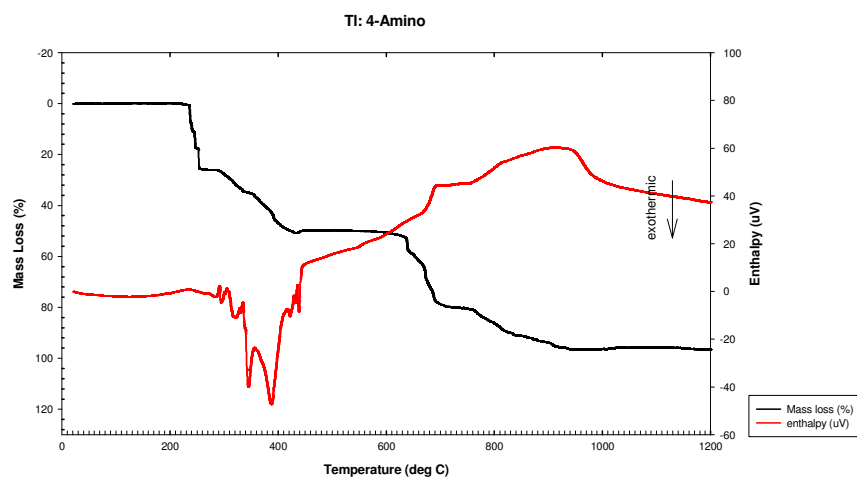


Fig. 6.2 4-amino complex without thiourea

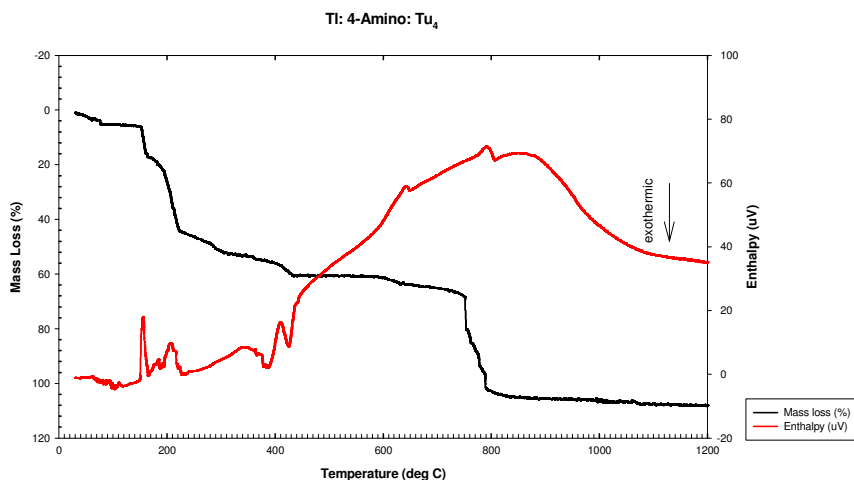


Fig. 6.3 4-amino complex (with thiourea)

Further evidence to substantiate that the peaks in the range of RT - 200°C correspond to thiourea is seen in Fig. 6.4 which is a thermogram of pure thiourea.

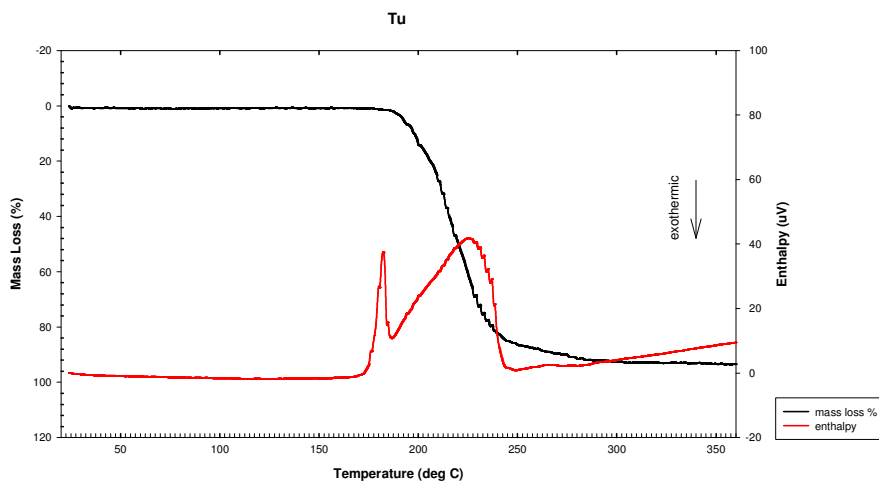


Fig. 6.4 Pure thiourea

As with the DSC results, some differences in the TG analysis exist. The TG analysis of 3-amino, 2-fluoro, 3-fluoro benzoates and the unsubstituted benzoate complexes as well as the 3 and 4-bromo complexes appear slightly different to the others. For these six complexes three distinct % mass losses are seen where as the majority of the other complexes have four % mass losses.

The first and largest mass loss coincides with the theoretical mass loss of all four thioureas (~200°C endothermic peak) and in some cases there also may well be

fragments of the aromatic ring. The second relatively small mass loss of approximately 8 % occurs in the temperature range of between approximately 240°C and 500°C and can be correlated to the loss of CO₂ from the complex. Two exceptions are the 2-nitro and 3-nitro complexes which show a mass loss of 19.2 % and 18.6 % respectively. These results can possibly be attributed to the loss of the NO₂ substituent as the combination of the loss of CO₂ and NO₂ fits the two values observed experimentally, however, this could not be proven. Of course one would expect the 4-nitro complex to follow this trend, however the NO₂ must be lost at a different temperature as only the loss of CO₂ is seen. As with the loss of thiourea, this can be shown by means of the mass spectroscopy results.

The final mass loss coincides with the endothermic peak at ~800°C and relates to the loss of the majority of the thallium as well as some organic residue associated with fragmentation of the substituted aromatic ring, hence the reason why the theoretical mass loss of the thallium is substantially lower than the actual mass loss. It was also proved by mass spectroscopy that some (minor) thallium is already removed at temperatures below 800°C.

Some thermographs suggested that the release of the four thiourea molecules is a two step process (1 + 3 TU), the analysis of the process by mass spectroscopy showed a continuous loss of thiourea from 30°C to 190°C. When the 2-fluoro sample was subjected to analysis with a METTLER TOLEDO TGA/SDTA 851e it was observed that the first step of the loss of one thiourea did not lead to a separate intermediate product containing the remaining three thiourea molecules. But the loss of the remaining 3 thiourea molecules was rather continuous.

The only complexes whose theoretical mass losses of thiourea did not coincide with the actual mass losses were the 2-fluoro, 3-bromo and 4-methoxy complexes. As stated above this was most likely due to the loss of aromatic fragments in this range.

The following shows the actual % mass losses for each complex along with what molecules come off. In brackets are the theoretical % mass losses.

COMPLEX	MASS LOSS %	MOLECULE/FRAGMENT (theoretical mass loss %)		
2-AMINO	12	1 Thiourea (12)		
	34	3 Thiourea (35)		
	8	CO ₂ (7)		
	44	Tl + some organic residue		
3-AMINO	51	4 Thiourea (47)		
	12	CO ₂ (7)		
	36	Tl + some organic residue		
4-AMINO	12	1 Thiourea (12)		
	37	3 Thiourea (35)		
	10	CO ₂ (7)		
	40	Tl + some organic residue		
2-NITRO	11	1 Thiourea (11)		
	36	3 Thiourea (34)		
	19	CO ₂ + NO ₂ (14)		
	52	Tl + some organic residue		
3-NITRO	16	1 Thiourea (11)	51	4 Thiourea (45)
	35	3 Thiourea (34)		
	18	CO ₂ + NO ₂ (14)		
	50	Tl + some organic residue		
4-NITRO	5	1 Thiourea (11)	39	4 Thiourea (45)
	34	3 Thiourea (34)		
	7	CO ₂ (7)		
	45	Tl + some organic residue		

2-FLUORO	63	4 Thiourea (47)		
	9	CO ₂ (7)		
	40	Tl + some organic residue		
3-FLUORO	52	4 Thiourea (47)		
	13	CO ₂ (7)		
	35	Tl + some organic residue		
4-FLUORO	9	1 Thiourea (12)	} 45	4 Thiourea (47)
	36	3 Thiourea (35)		
	8	CO ₂ (7)		
	45	Tl + some organic residue		
2-BROMO	9	1 Thiourea (11)		
	34	3 Thiourea (32)		
	8	CO ₂ (6)		
	41	Tl + some organic residue		
3-BROMO	59	4 Thiourea (43)		
	7	CO ₂ (6)		
	33	Tl + some organic residue		
4-BROMO	46	4 Thiourea (43)		
	8	CO ₂ (6)		
	43	Tl + some organic residue		

2-CHLORO	6	1 Thiourea (12)	44	4 Thiourea (46)
	38	3 Thiourea (34)		
	6	CO ₂ (7)		
	43	Tl + some organic residue		
3-CHLORO	6	1 Thiourea (12)	48	4 Thiourea (46)
	42	3 Thiourea (34)		
	7	CO ₂ (7)		
	37	Tl + some organic residue		
4-CHLORO	4	1 Thiourea (12)	46	4 Thiourea (46)
	42	3 Thiourea (34)		
	10	CO ₂ (7)		
	42	Tl + some organic residue		
2-METHYL	11	1 Thiourea (12)		
	36	3 Thiourea (36)		
	7	CO ₂ (7)		
	43	Tl + some organic residue		
3-METHYL	7	1 Thiourea (12)	49	4 Thiourea (47)
	42	3 Thiourea (36)		
	4	CO ₂ (7)		
	52	Tl + some organic residue		
4-METHYL	12	1 Thiourea (12)		
	36	3 Thiourea (36)		
	8	CO ₂ (7)		
	45	Tl + some organic residue		

2-HYDROXY	5	1 Thiourea (12)	} 47	4 Thiourea (47)
	43	3 Thiourea (36)		
	9	CO ₂ (7)		
	43	Tl + some organic residue		
4-METHOXY	5	1 Thiourea (12)	} 35	3 Thiourea (35)
	30	3 Thiourea (35)		
	4	CO ₂ (7)		
	59	Tl + some organic residue		
BENZOATE	53	4 Thiourea (48)		
	4	CO ₂ (7)		
	33	Tl + some organic residue		

Table 6.2 Table showing mass losses, molecules and fragments coming off, and theoretical mass losses (%).

Elemental analysis of the thallium and sulphur content for a selection of ten complexes of which sufficient material were available produced an average ratio of 1:3[6]. The 3-fluoro complex was the only complex with known 1:4 ratio included in these samples and this correct ratio was indeed observed. It must be stated that the physical quality of all the other complexes in general deteriorated upon recrystallisation. Unfortunately it was no longer possible to resynthesise these complexes in sufficient quantity as required for the analysis (5 g of each). Although it is known that some of these complexes do not necessarily have a 1:4 ratio, these results are inconclusive .

6.6 MASS SPECTROMETRY

In order to fully interpret the results obtained from the thermal analysis techniques, some of the complexes were analysed using mass spectrometry obtained over the temperature range corresponding to the observed thermal events. The procedure involved heating the samples to temperatures which coincided with large % mass losses in the TG and at these temperature ranges record the mass spectra to obtain information of the decomposition process.

Due to the fact that all the thermal results were very similar, the 2-fluoro complex was analysed as a representation of the complexes, also with the aim of clarifying the mass loss associated with the loss of thiourea.

As can be seen from the mass spectrum, the thiourea ($m/z = 76$) is visible at 30°C, at 150°C its abundance has decreased substantially and by 190°C it is completely gone. These results correspond to the TG results which show a mass loss of 63 % in and around the same temperature. It should be noted that the mass loss value of 63 % is higher than the expect value for the loss of four thiourea, 47 %. Due to this large difference, the sample was rerun on the accurate thermal software (see experimental) and a mass loss of 57 % was obtained. This result firstly proves the definite inaccuracies associated with the thermal instrumentation used (as discussed in the experimental) and secondly implies that this mass loss must include aromatic fragments as well as the thiourea.

It is worth noting that the relative masses of both thiourea and C_6H_4 (the aromatic ring) are 76, however, the mass spectroscopy software used was able to give the accurate masses and confirm that the peak at 76 did in fact relate to the thiourea.

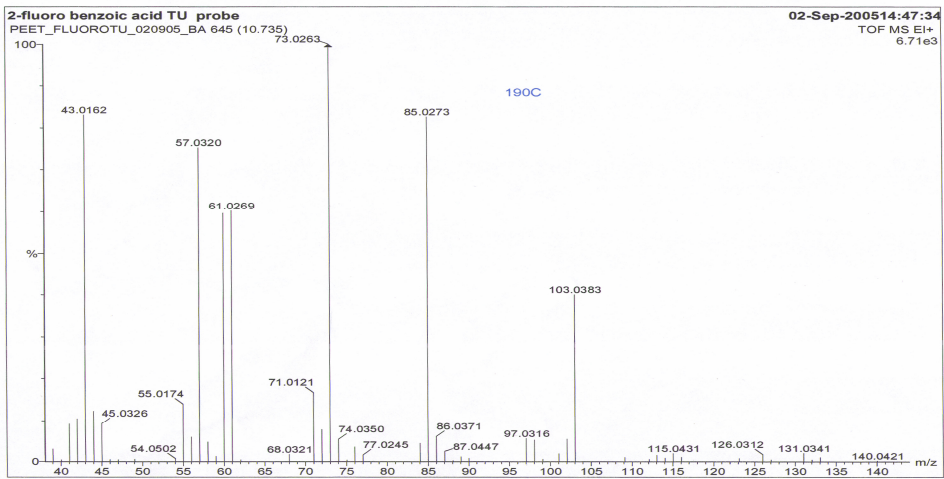
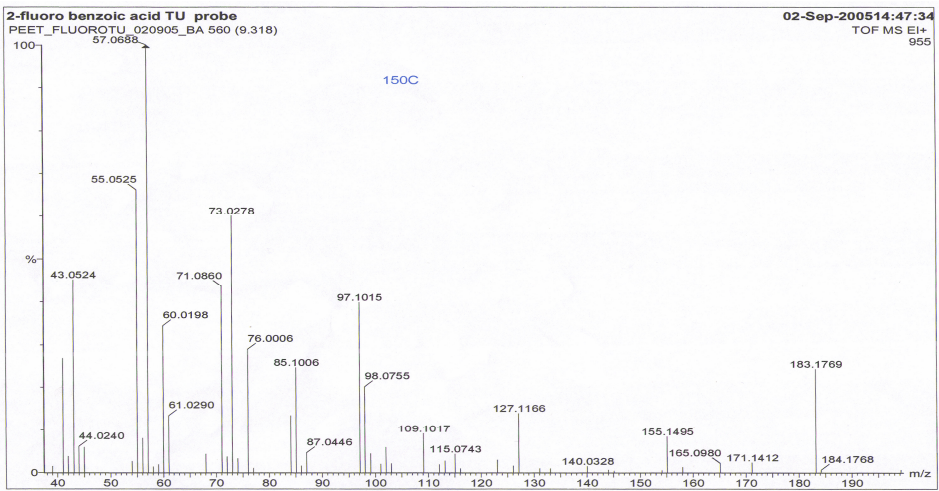
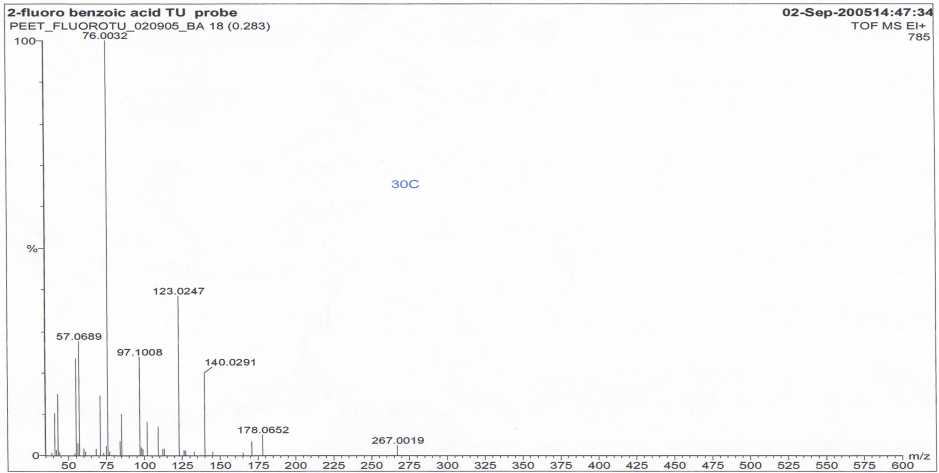


Fig. 6.5 Mass spectra of 2-fluoro at 30°C, 150°C and 190°C showing the loss of thiourea

At 350°C the CO₂ (m/z = 44) is visible (confirmed by the accurate mass given by the software) and corresponds to the second mass loss in the TG results.

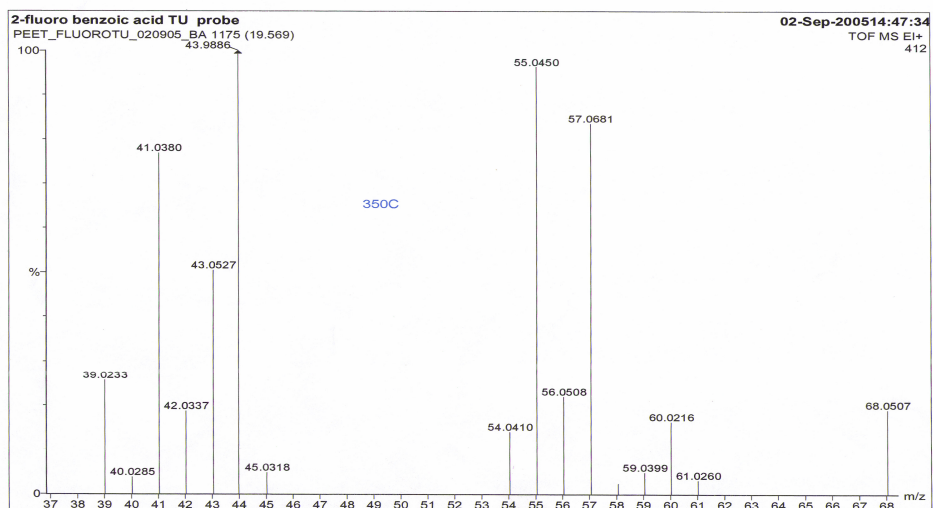


Fig. 6.6 Mass spectrum of 2-fluoro at 350°C showing the presence of CO₂

Above 550°C the Thallium (m/z = 205) is visible (confirmed by the accurate mass given by the software) and corresponds to the third mass loss in the TG results.

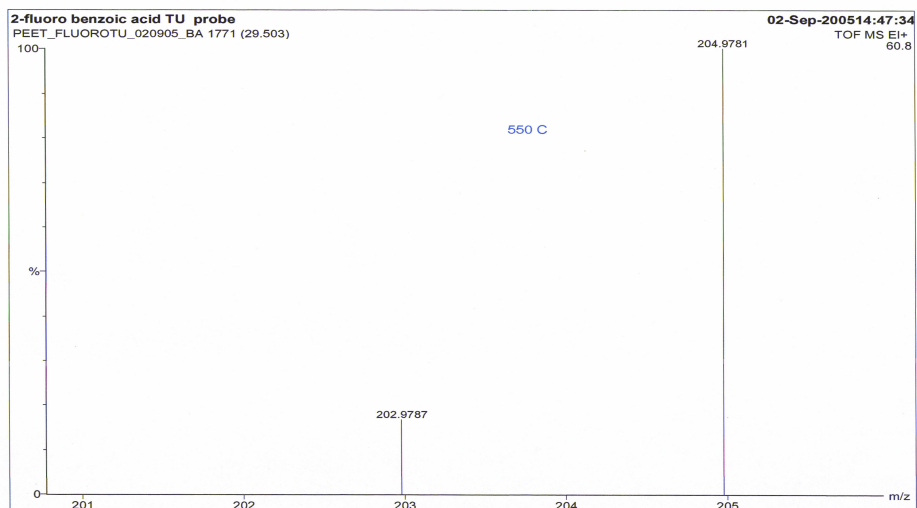


Fig. 6.7 Mass spectrum of 2-fluoro at 550°C showing the presence of Tl

5.7 MELTING POINTS OF COMPLEXES

It is important to note that the melting points of the complexes were obtained in two ways. Firstly, by the simple method of heating the complex on a hot plate with a thermometer attached and watching for the exact point of melting using a microscope. Secondly, by simply looking at the DSC results and noting the temperature that the first peak appears. As expected the two set of results are not exactly the same due to human and experimental error but they are most certainly in the same approximate range.

MELTING POINTS OBTAINED FROM MELTING POINT INSTRUMENT

COMPLEX	MELTING POINT (°C)
Tl-2-aminobenzoate-thiourea	166.7-170.7
Tl-3-aminobenzoate-thiourea	216.6-219.7 *
Tl-4-aminobenzoate-thiourea	169.7-172.8
Tl-2-nitrobenzoate-thiourea	163.2-167.5
Tl-3-nitrobenzoate-thiourea	178.8-183.2
Tl-4-nitrobenzoate-thiourea	179.8-181.3
Tl-2-fluorobenzoate-thiourea	208.0-209.8 *
Tl-3-fluorobenzoate-thiourea	205.3-206.1 *
Tl-4-fluorobenzoate-thiourea	185.0-188.3
Tl-2-bromobenzoate-thiourea	163.0-167.8
Tl-3-bromobenzoate-thiourea	190.6-192.3
Tl-4-bromobenzoate-thiourea	188.5-190.0
Tl-2-chlorobenzoate-thiourea	161.1-164.3
Tl-3-chlorobenzoate-thiourea	189.5-191.1
Tl-4-chlorobenzoate-thiourea	182.6-188.9
Tl-2-methylbenzoate-thiourea	165.2-168.7
Tl-3-methylbenzoate-thiourea	178.4-180.8
Tl-4-methylbenzoate-thiourea	175.6-179.4
Tl-4-methoxybenzoate-thiourea	163.2-167.0
Tl-2-hydroxybenzoate-thiourea	179.5-184.3
Tl-benzoatebenzoate-thiourea	211.2-212.5 *

Table 6.3 Melting points of complexes * denotes single crystal structure obtained

Of great importance is to note that the four complexes marked with * in Table 6.3 and Fig. 6.8 yielded very similar single crystal structures and these compounds have melting points in a distinct temperature range that differs from the rest. No usable single crystals of any of the other complexes could be obtained even after many recrystallisation experiments.

6.8 MELTING POINTS OF ALL COMPLEXES

The melting point values used in the graph below were obtained from melting point instrument (hotplate, thermometer and microscope) and not from DSC.

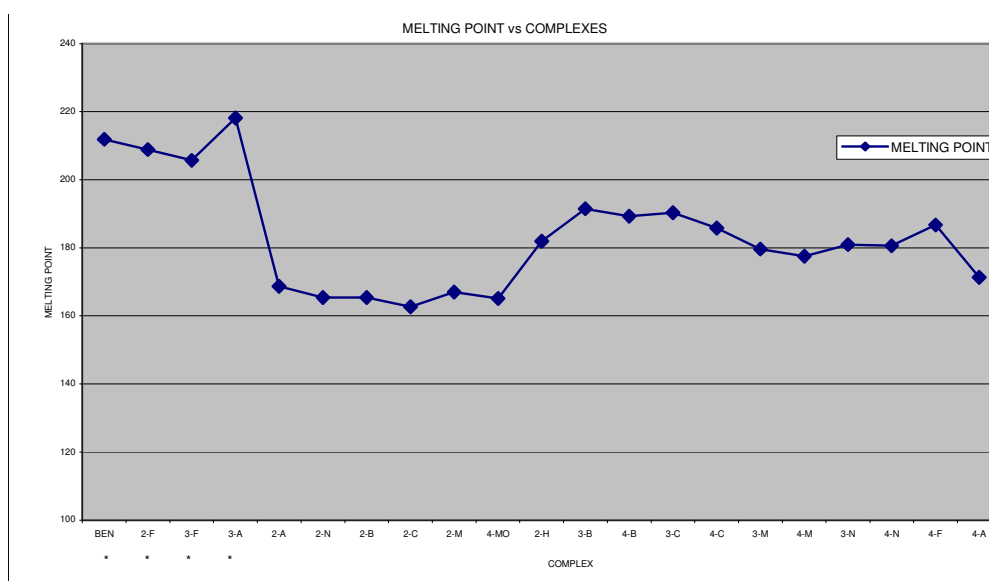


Fig. 6.8 Graph to show melting point vs molecular weight where the x axis scale relates to the 1st letter of the substituted complexes.

It can be seen from the graph above that the melting points of all the synthesized complexes can be classified into three categories. Firstly, the 3-amino, 2-fluoro, 3-fluoro, benzoate complexes which produced good single crystals have the highest melting points (218.2°C, 208.9°C, 211.9°C, 205.7°C respectively).

Of the remaining complexes the ortho substituted complexes, barring the 2-hydroxy complex, have similar melting points in the narrow region of 162.7-168.7°C.

It should be noted that the 2-hydroxy complex is involved in increased hydrogen bonding within the complex, hence the higher melting point. This can be seen in the IR spectrum where the normally sharp OH band at above 3600 cm^{-1} is not seen but has instead shifted to a lower wavenumber due to hydrogen bonding [7]. However, the band is not seen as it has shifted to the region where the thiourea bands are most prominent and so it is masked. Also included in this category is the 4-methoxy complex with a melting point of 165.1°C . This may be due to the non-planarity of the methoxy substituent relative to the benzene ring.

The third category is the remaining meta and para substituted complexes. Although the overall melting point range of this grouping is rather large, the meta and para positions of the same substituent complexes have very similar melting points, i.e. 3- and 4-nitro, 3- and 4-bromo, etc. The one exception being the 4-fluoro complex.

Of significance is the fact that three of the four complexes that produced diffraction quality single crystals (2-fluoro complex, 3-fluoro complex and benzoate complex) have very narrow melting point ranges which may also be an indication that they are indeed more crystalline than the other complexes. As some of the other complexes were repeatedly re-crystallized it was accepted that the wider range do not necessarily reflect a less pure complex.

6.9 MELTING POINT vs MOLECULAR WEIGHT

Melting points increase with increasing molecular weight as polarisability increases with increasing number of electrons and the number of electrons is in a general way related to the molecular weight. (Polarisability is the ease with which a dipole can be induced in an atom or molecule due to electron charge distortion.) [8]. However, there are both strong ionic and other dipole interactions present in these complexes as well.

The table shows that although the complexes of the same molecular weight have roughly the same melting point, there is no trend which shows melting point increasing with increased molecular weight.

6.10 CONCLUSION

The TG and DSC techniques that were used provided good results which complimented each other in terms of exothermic and endothermic peaks of the DSC occurring in the same regions as the various % mass losses of the TG.

The main conclusions made were as follows:

- The four crystal structures (2-fluoro, 3-fluoro, 3-amino and benzoate complexes) showed comparable enthalpy values associated with the loss of four thiourea molecules. These four values were the highest observed in the group of six highest enthalpy readings. The remaining two complexes were a 2-methyl and a 3-bromo derivative. This also supports the suggestion by the crystallographic results that a more bulky substituent on the 3-position could be accommodated in that existing packing.
- It must be noted that the difference in enthalpy values for the 4-amino and the 4-nitro complexes is very large. The 4-amino complex has a 3 times higher enthalpy value, most likely due to the electron donating character of the amino group resulting in stronger hydrogen bonding when compared with the electron withdrawing effect of the nitro group.
- It is not clear why the 2-amino complex has such a lower enthalpy value than that of the 2-methyl complex. It could be expected that there are small differences in the relative size of these two functional groups, however, the stronger electron donating properties of the amino group does not seem to affect the enthalpy values.
- The 3-bromo and 2-methyl complexes also showed comparable enthalpy values related to the loss of four thiourea molecules. The values were slightly lower than those observed for the four benzoates above, but significantly higher than the rest of the complexes. This may indicate the same type of bonding and or packing strength as for the four benzoates above.
- The remaining complexes differed with no other clear identifiable groupings. However, the group of eight complexes with similar powder diffraction patterns include two of the complexes with the lowest enthalpy values (4-nitro and 4-methoxy).

- It was proven that the four thiourea molecules are released first as confirmed by the mass spectroscopy.

It can also be concluded that varying the substituent on the benzene ring according to different electronic properties does not have any effect on the thermal events that take place in the complexes.

In addition to the two thermal techniques used, the mass spectrometry worked well along side them to give a deeper understanding of the data obtained.

6.11 REFERENCES

CHAPTER 6

1. J. W. Dodds and K. H. Tonge, Thermal Methods, Wiley, 1987, page 1-166
2. www.anasys.co.uk/library/tga1, page 3
3. J. W. Dodds and K. H. Tonge, Thermal Methods, Wiley, 1987, page 5
4. J. W. Robinson, Undergraduate Instrumental Analysis, 1987, pages 483, 492-496
5. S. El-Houte, M. El-Sayed Ali and O. Toft Sorensen, Thermochemica Acta, 1989, **138**, 107-114
6. Professional analysis by Setpoint Holding Company, SPL Report number 5/1976
7. D. Lin-Vien, N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, Boston, MA, 1991, page 47
8. R. H. Petrucci, General Chemistry, 5th ed., 1989, pages 410-414

6.12 THERMAL DATA OF ALL THE COMPLEXES

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
2-AMINO COMPLEX	145 endo 170 endo 193 endo 360 exo 407 exo 636 endo 790 endo	25-166 166-307 307-460 460-857	12 34 8 44
3-AMINO COMPLEX	210 endo 389 exo 473 exo 638 endo 753 endo	184-425 425-565 565-869	51 12 36
4-AMINO COMPLEX	151 endo 170 endo 194 endo 361 exo 411 exo 632 endo 780 endo	79-176 176-368 368-703 703-655	12 37 10 40

Table 6.4 Thermal data including DSC/DTA results, TG results and mass loss for the 2/3/4 amino complexes

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
2-NITRO	151 endo	45-160	11
COMPLEX	170 endo	160-241	36
	200 endo	241-470	19
	355 exo	470-946	52
	405 exo		
	631 endo		
	790 endo		
3-NITRO	150 exo	41-178	16
COMPLEX	173 endo	178-269	35
	198 endo	269-489	19
	367 exo	489-880	50
	435 exo		
	627 endo		
	774 endo		
4-NITRO	154 endo	59-174	5
COMPLEX	173 endo	174-472	34
	197 endo	472-606	7
	379 exo	606-913	45
	480 exo		
	630 endo		
	762 endo		

Table 6.5 Thermal data including DSC/DTA results, TG results and mass loss for the 2/3/4 nitro complexes

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
2-FLUORO	204 endo	184-249	63
COMPLEX	356 exo	249-447	9
	406 exo	447-878	40
	645 endo		
	838 endo		
3-FLUORO	195 endo	199-245	52
COMPLEX	360 exo	245-444	13
	420 exo	444-904	35
	472 exo		
	640 endo		
	820 endo		
4-FLUORO	152 endo	62-179	9
COMPLEX	180 endo	179-434	36
	189 endo	434-690	8
	205 endo	690-897	45
	347 exo		
	395 exo		
	638 endo		
	800 endo		

Table 6.6 Thermal data including DSC/DTA results, TG results and mass loss for the 2/3/4 fluoro complexes

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
2-CHLORO COMPLEX	150 endo	96-170	6
	183 endo	170-332	38
	203 endo	332-458	6
	367 exo	458-867	43
	402 exo		
	635 endo		
	809 endo		
3-CHLORO COMPLEX	139 exo	55-175	6
	185 endo	175-272	42
	205 endo	272-425	7
	343 exo	425-835	37
	383 exo		
	632 endo		
	777 endo		
4-CHLORO COMPLEX	158 endo	139-173	4
	181 endo	173-272	42
	190 endo	272-451	10
	202 endo	451-860	42
	362 exo		
	400 exo		
	635 endo		
	800 endo		

Table 6.7 Thermal data including DSC/DTA results, TG results and mass loss for the 2/3/4 chloro complexes

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
2-BROMO	140 endo	68-171	9
COMPLEX	165 endo	171-338	34
	194 endo	338-434	8
	350 exo	434-917	41
	394 exo		
	634 endo		
	791 endo		
3-BROMO	192 endo	169-244	59
COMPLEX	342 exo	244-660	7
	386 exo	660-1154	33
	630 endo		
	750 endo		
4-BROMO	188 endo	152-267	46
COMPLEX	195 endo	267-453	8
	370 exo	453-862	43
	420 exo		
	640 endo		
	802 endo		

Table 6.8 Thermal data including DSC/DTA results, TG results and mass loss for the 2/3/4 bromo complexes

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
2-METHYL COMPLEX	150 endo	126-179	11
	182 endo	179-318	36
	356 exo	318-471	7
	411 exo	471-880	43
	638 endo		
	831 endo		
3-METHYL COMPLEX	141 exo	32-147	7
	175 endo	147-384	42
	201 endo	384-486	4
	354 exo	486-946	52
	400 exo		
	641 endo		
	799 endo		
4-METHYL COMPLEX	158 endo	101-173	12
	173 endo	173-317	36
	192 endo	317-432	8
	398 exo	432-841	45
	621 endo		
	770 endo		

Table 6.9 Thermal data including DSC/DTA results, TG results and mass loss for the 2/3/4 methyl complexes

COMPLEX	DSC/DTA results T peak (°C)	TG results T range (°C)	Mass loss (%)
4-METHOXY COMPLEX	145 endo	25-173	5
	190 endo	173-313	30
	376 exo	313-568	4
	431 exo	568-1002	59
	640 endo		
	803 endo		
2-HYDROXY COMPLEX	142 exo	106-156	5
	176 endo	156-361	43
	192 endo`	361-490	9
	375 exo	490-919	43
	415 exo		
	626 endo		
	791 endo		
BENZOATE COMPLEX	207 endo	185-238	53
	340 exo	238-418	4
	370 exo	418-878	33
	634 endo		
	730 endo		

Table 6.10 Thermal data including DSC/DTA results, TG results and mass loss for the 4-methoxy, 2-hydroxy and benzoate complexes

6.13 TG AND DSC SPECTRA

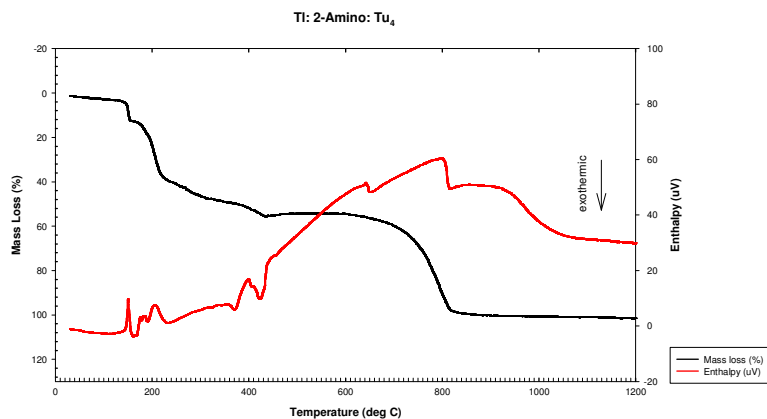


Fig. 6.9 TG and DSC spectrum of the 2-amino complex

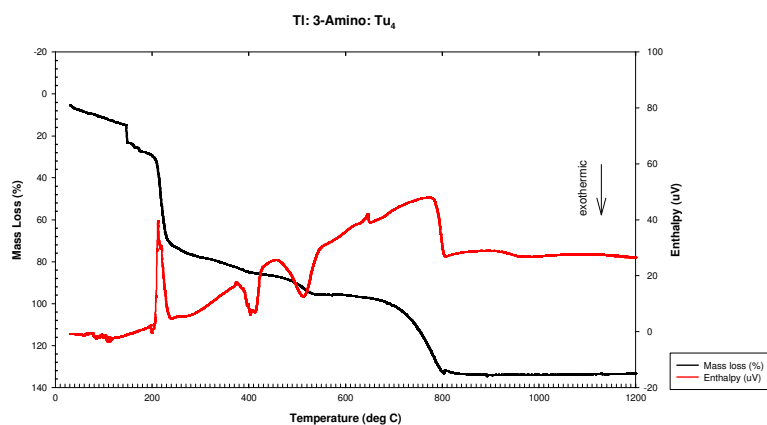


Fig. 6.10 TG and DSC spectrum of the 3-amino complex

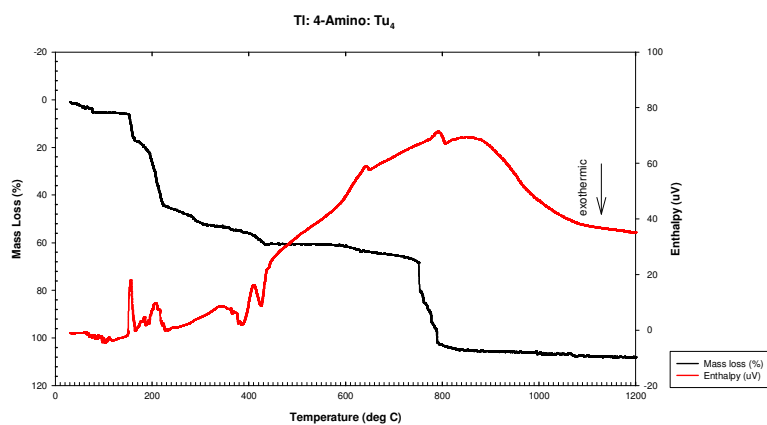


Fig. 6.11 TG and DSC spectrum of the 4-amino complex

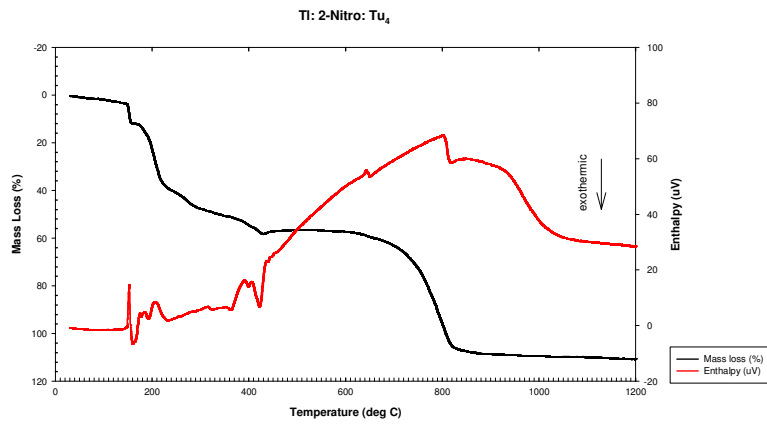


Fig. 6.12 TG and DSC spectrum of the 2-nitro complex

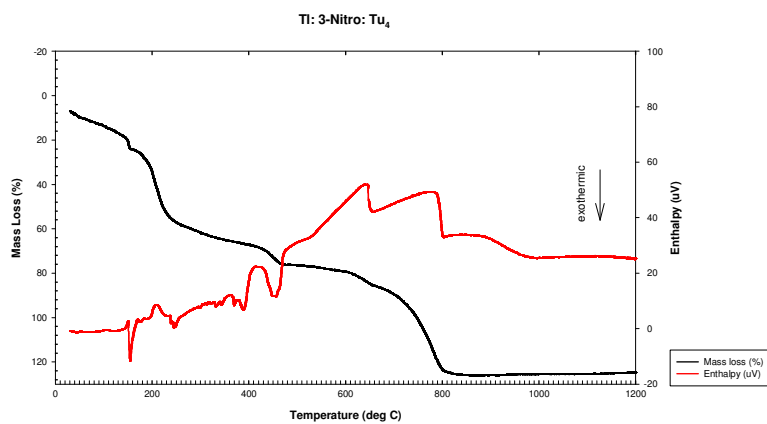


Fig. 6.13 TG and DSC spectrum of the 3-nitro complex

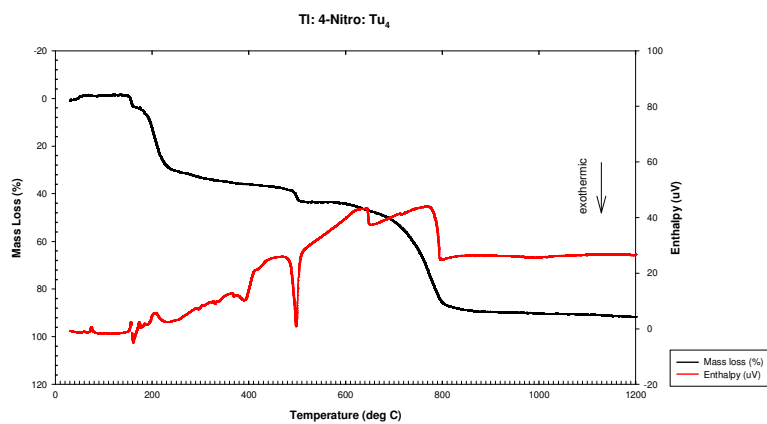


Fig. 6.14 TG and DSC spectrum of the 4-nitro complex

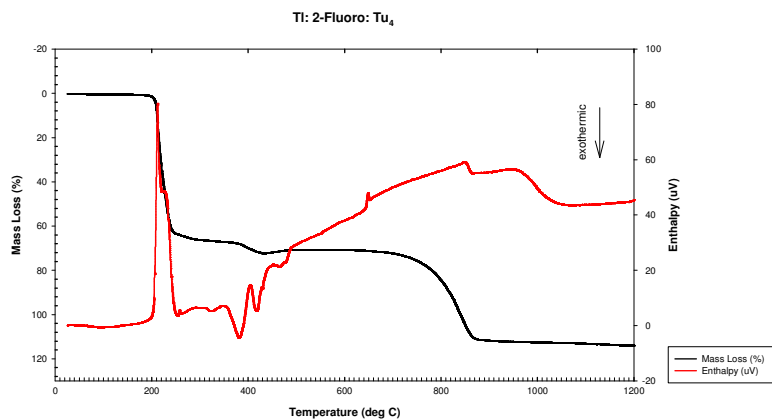


Fig. 6.15 TG and DSC spectrum of the 2-fluoro complex

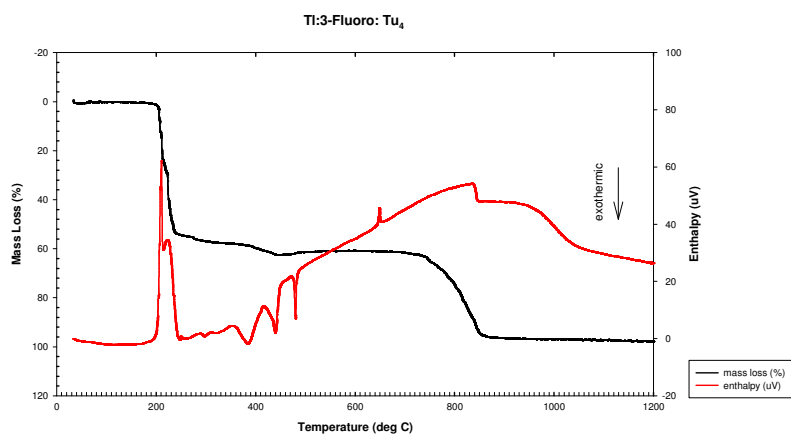


Fig. 6.16 TG and DSC spectrum of the 3-fluoro complex

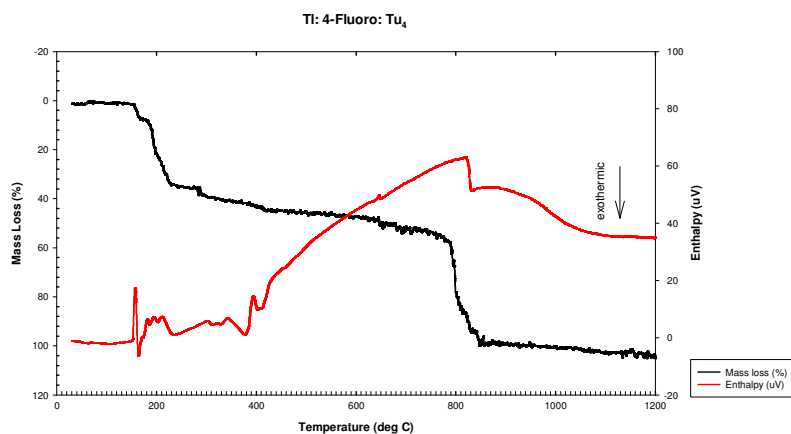


Fig. 6.17 TG and DSC spectrum of the 4-fluoro complex

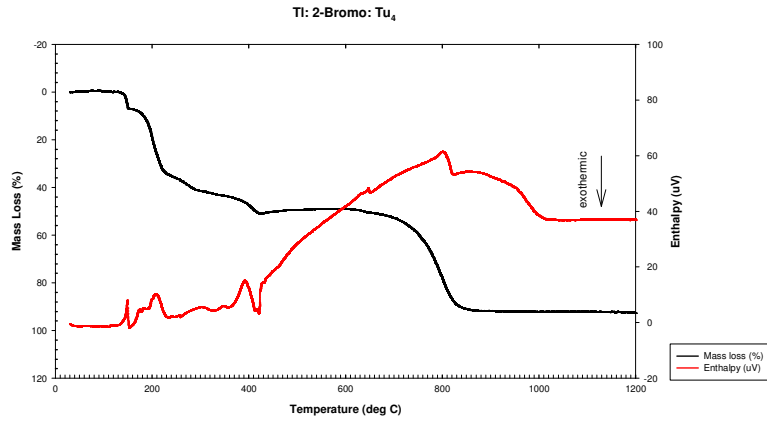


Fig. 6.18 TG and DSC spectrum of the 2-bromo complex

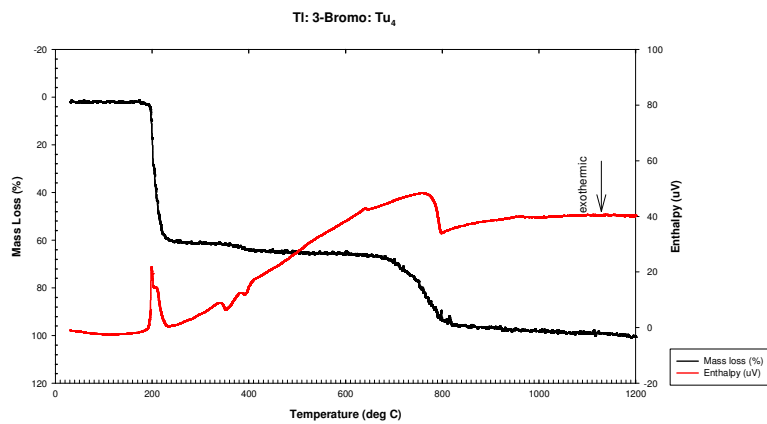


Fig. 6.19 TG and DSC spectrum of the 3-bromo complex

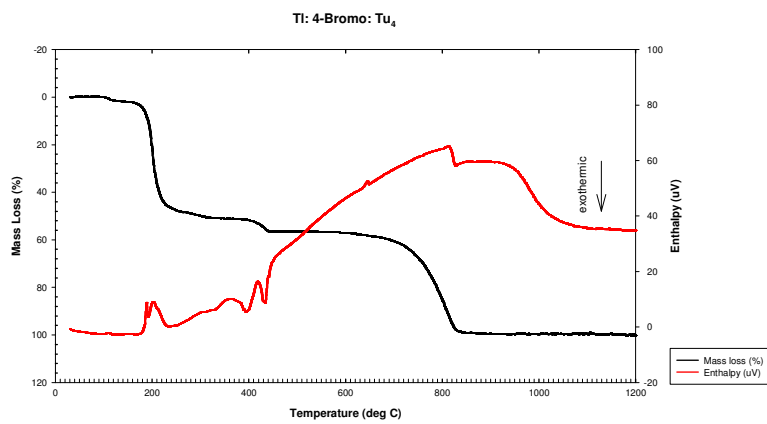


Fig. 6.20 TG and DSC spectrum of the 4-bromo complex

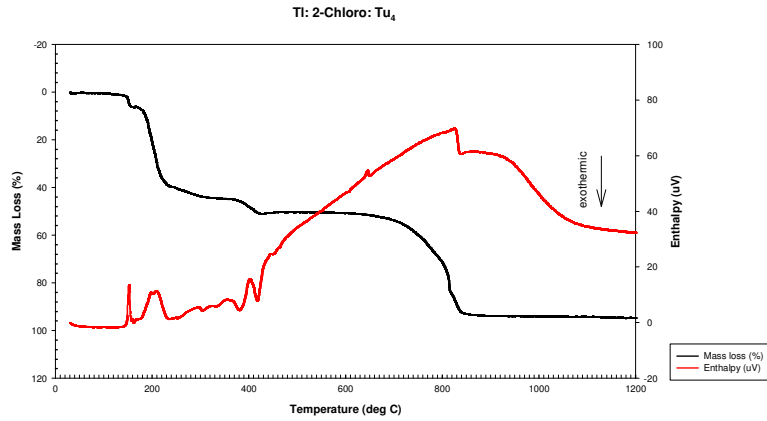


Fig. 6.21 TG and DSC spectrum of the 2-chloro complex

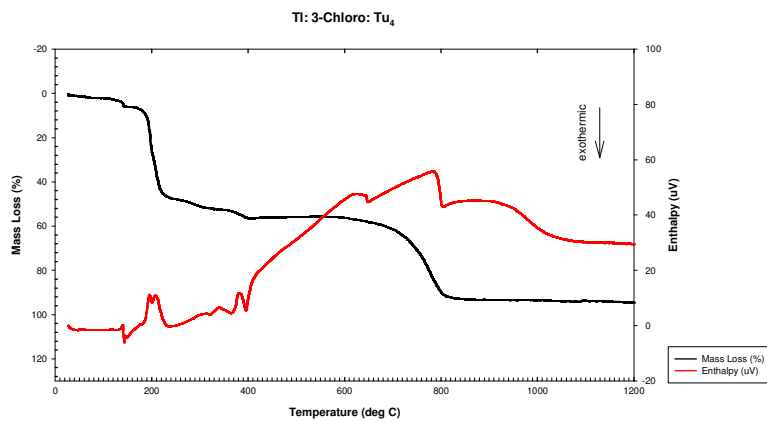


Fig. 6.22 TG and DSC spectrum of the 3-chloro complex

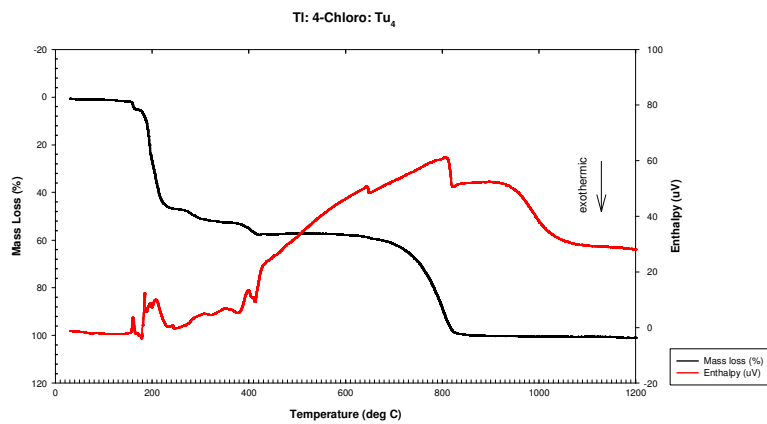


Fig. 6.23 TG and DSC spectrum of the 4-chloro complex

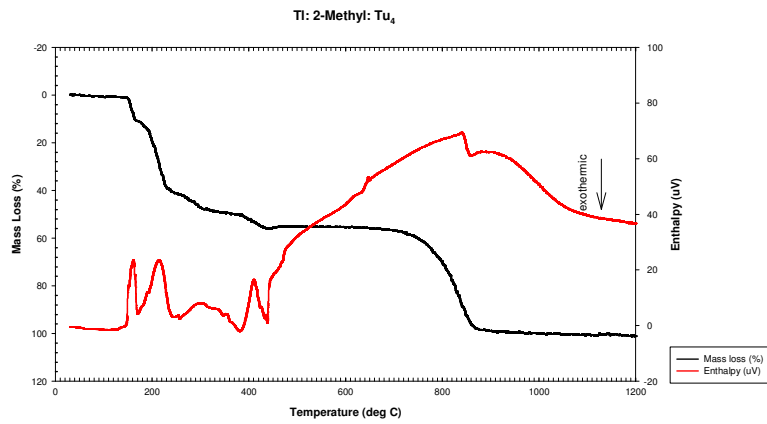


Fig. 6.24 TG and DSC spectrum of the 2-methyl complex

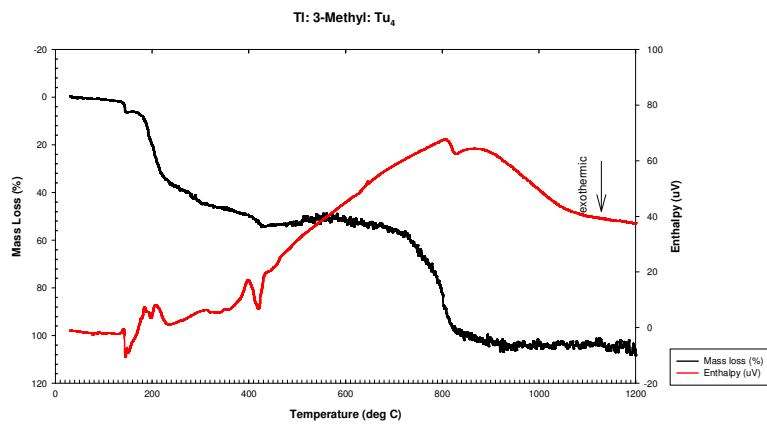


Fig. 6.25 TG and DSC spectrum of the 3-methyl complex

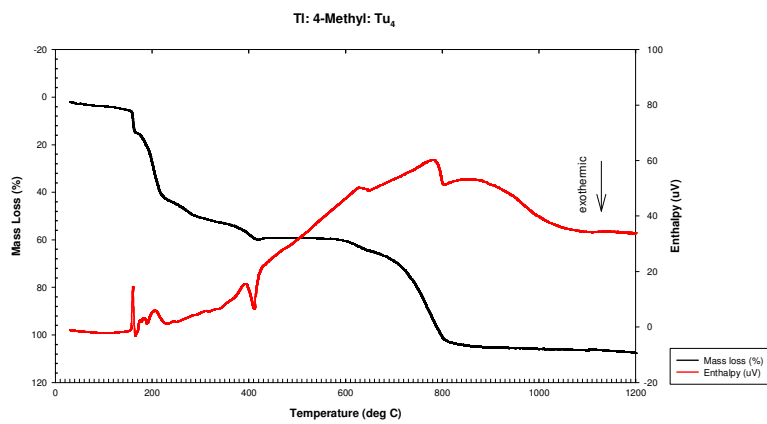


Fig. 6.26 TG and DSC spectrum of the 4-methyl complex

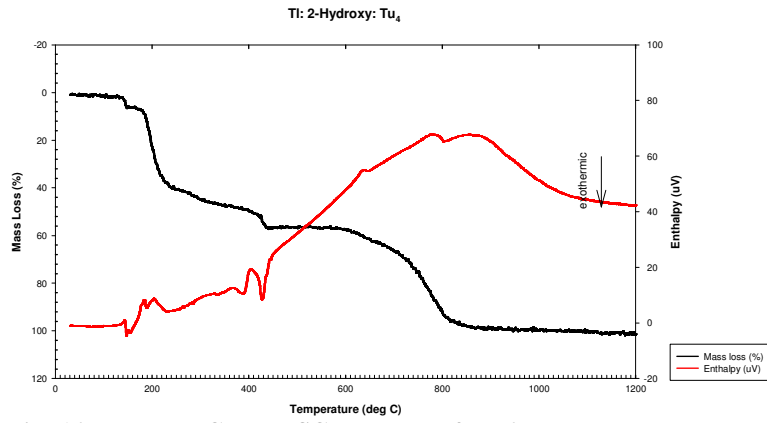


Fig. 6.27 TG and DSC spectrum of the 2-hydroxy complex

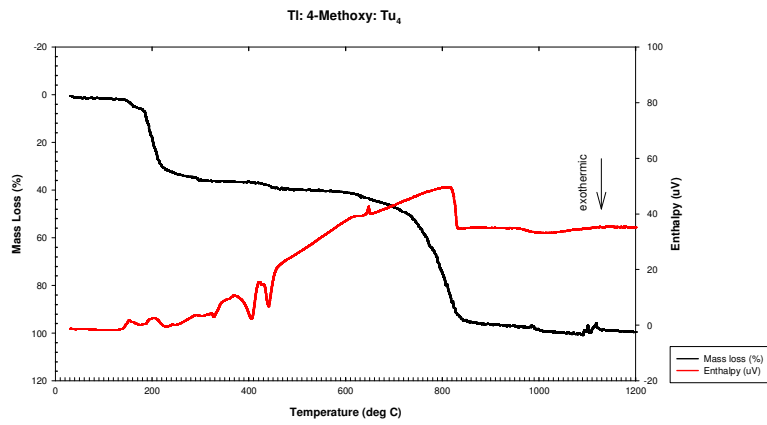


Fig. 6.28 TG and DSC spectrum of the 4-methoxy complex

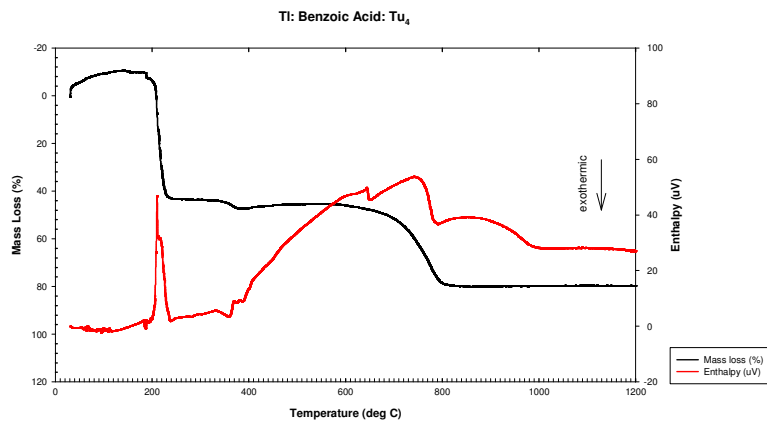


Fig. 6.29 TG and DSC spectrum of the benzoate complex