CHAPTER 3

INFRARED AND RAMAN SPECTROSCOPY

3.1 INTRODUCTION

Raman and infrared spectroscopy measure the energy difference between vibrational energy levels in molecules. The main difference between these two spectroscopic techniques is that IR active vibrations cause a change in the dipole moment of the molecule, whereas a vibration is Raman active if it changes the molecular polarizability. Therefore, whether or not a vibrational mode is active or inactive depends on the symmetry of the molecules [1].

The position of a given stretch vibration in both Raman and infrared spectra can be related to two factors namely the masses of the atoms involved (light atoms vibrate at higher frequencies than heavier ones) and the relative strength of the bond. The wavenumber position of a specific vibration associated with a bond between the same atoms therefore decrease in the following order $sp>sp^2> sp^3$.

Furthermore the position of a vibrational mode is dependent on the environment of a molecule. Molecular substituents, molecular geometry and hydrogen bonding affect the vibrational force constant, which dictates the vibrational energy (position of band).

Infrared and Raman spectroscopy are therefore useful methods to study intermolecular interactions and can give useful information about the geometry of crystalline compounds, as both methods are sensitive to changes in bond lengths and symmetry of molecules. Furthermore the formation of new bonds upon complexation can be monitored through Raman and IR spectroscopy by the appearance of new bands in the spectra.

In the complexes under study the polarizable thiourea ligands act as bridges between the separated anions and cations. Vibrational spectra of the thiourea ligand are sensitive to structural changes and have been used extensively to obtain more information about covalent metal-thiourea coordination compounds and thiourea inclusion compounds [6, 7]. The cation-thiourea columns are identical in all of the complexes, therefore the differences in crystal structure are a direct consequence of the ionic strength, size and morphology of the anions.

The FT-Raman and FTIR spectra of all the thiourea complexes were obtained and the spectra are used to illustrate the ionic nature of the intermolecular interactions and confirm the presence of hydrogen bonding in the complexes.

3.2 EXPERIMENTAL DETAIL

The instrumentation used to collect the required transmission infrared vibrational data was a Perkin Elmer Spectrum RX-1, FT-IR System. The analysis was carried out in the solid state. 2 mg of each complex and ~100 mg KBr powder were grounded together using a pestle and mortar until a fine homogeneous powder remained. The KBr is used as a diluting agent, as it does not absorb above 250 cm^{-1} [2] which means that all bands seen in the spectrum relate to the complex. The fine powder is then pressed using a hydraulic press until a clear pellet is produced for analysis. In each interferogram 32 scans were signal averaged, with a spectral resolution of 4 cm^{-1}.

In order to reduce the fluorescence experienced with 514.5 nm laser excitation, a FT-Raman Spectrometer was used which contained an Nd:YAG laser to excite the Raman effect. The Nd:YAG laser has a wavelength of 1064 nm and at this wavelength there are less electronic transitions [3], which in many instances are responsible for a high fluorescence background. The laser power was 500 mW and 512 scans were accumulated with a resolution of 4 cm^{-1}.

As with the IR experiments, the analysis was carried out in the solid state, however, unlike the infrared studies there was very little sample preparation required. A small amount of each complex was placed in a test tube and loaded into the sample compartment. The only necessary and important factor to be considered is that the sample must be in the foci of the laser beam and collection lens [3].

Section 3.3 includes the analysis of the spectra obtained for thiourea (TU), benzoate complex $[(C_6H_5COO)Tl\cdot 4(SCN_2H_4)]$, 3-amino complex $[(C_6H_6NCOO)Tl\cdot 4(SCN_2H_4)]$, 2-fluoro complex $[(C_6H_4FCOO)Tl\cdot 4(SCN_2H_4)]$ and the 3-fluoro complex $[(C_6H_4FCOO)Tl\cdot 4(SCN_2H_4)]$. These four complexes were the only complexes where accurate structural data was obtained (see Chapter 2), thus allowing the possibility to correlate the crystallographical and spectroscopic data. The assignments of the bands for the other complexes was guided by this analysis and information obtained in the literature and are given in 3.5 and 3.7.

3.3 DISCUSSION

According to past crystallographic studies carried out on [$(C_6H_5COO)Tl \cdot 4(SCN_2H_4)$], it is known that hydrogen bonding occurs between the oxygen atoms of the benzoate ions and the amino hydrogen atoms of the thiourea molecules [4]. Due to the preferred orientation in the packing of the complexes in the solid state there are two different N-H…O approaches, 2.92 Å and 3.03 Å. These are discussed in greater depth in the crystallographic chapter, but suffice to say those of 2.92 Å are stronger hydrogen bonds than those of 3.03 Å and may well be indicated in the spectra by a larger shift [4].

In IR and Raman spectra hydrogen bonding is observed mainly by a broadening of the spectral bands in question as well by a shift of the bands to lower frequencies [5].

It is indicated that some of the complexes that were synthesised are isostructural, and if this is true then the hydrogen bond distances will be very similar to the [$(C_6H_5COO)Tl \cdot 4(SCN_2H_4)$] and it is expected that the IR and Raman spectra of the complexes will be very similar.

In Figures 3.1 and 3.2 the FT-Raman and FT-IR spectra of four of the complexes and thiourea are presented. The complexes are the 2-fluoro, 3-fluoro, 3-amino benzoates and the unsubstituted benzoate, which were selected as they were the only complexes which produced single crystal diffraction quality crystals. These four complexes turned out to be isostructural (Chapter 2).

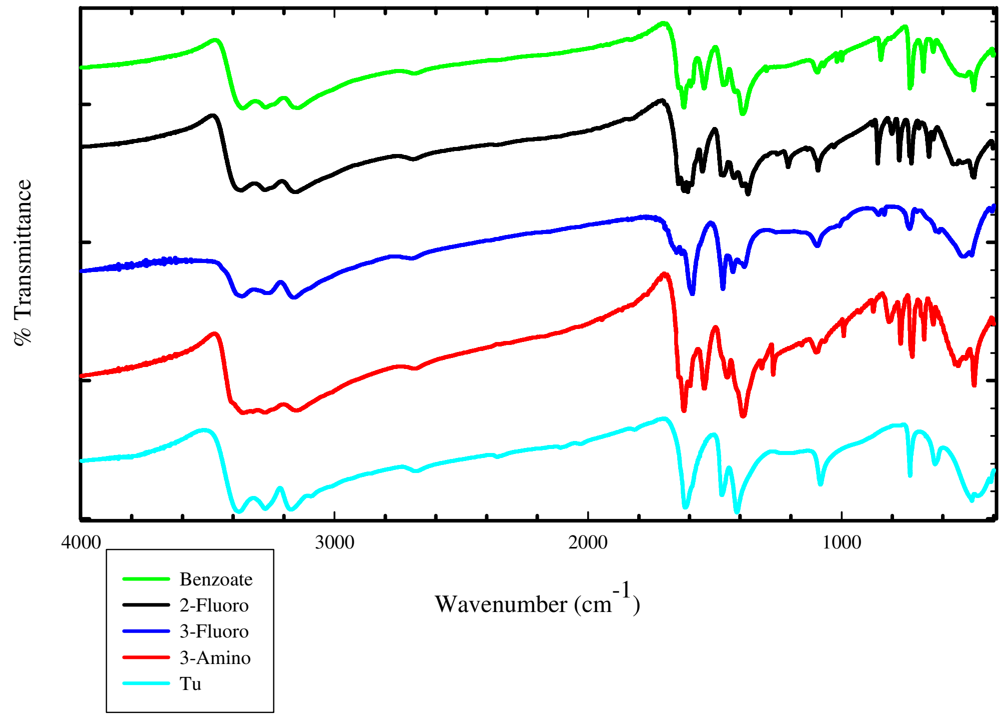
IR Full range comparison

Fig 3.1 IR spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea

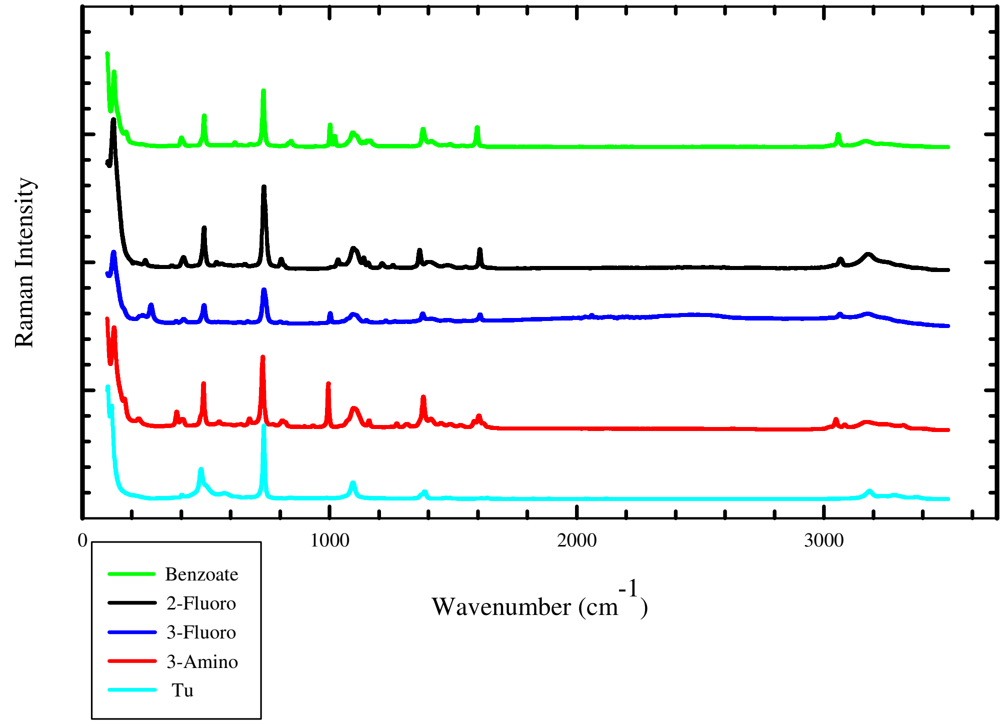
Raman Full comparison

Fig 3.2 Raman spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea

It is important to note that the C, N and S atoms of the thiourea molecule are co-planar and due to resonance structures the thiourea molecule has complex vibrational dynamics, arising from the mixture of its normal modes of vibration. Therefore, some contradictory interpretations and assignments of vibrational bands are found in the literature for thiourea and its complexes. The comprehensive assignments given in references [6, 7] were used throughout the chapter as these are the most thorough and complete thiourea IR and Raman references that were available.

In all the spectra (including those of the complexes that did not produce crystals suitable for single crystal analysis) the majority of the thiourea bands are in most instances easily identified as can be seen in Fig. 3.1 and 3.2.

It is not with in the scope of this study to do a full analysis of the very complex spectra of the benzoate anions, which is influenced by the position and type of substituents. The main focus is on the comparison of the thiourea bands in the coordination metal – thiourea complexes in order to study the hydrogen bonding, as well as the ionic nature of these complexes.

For convenience sake the FT-Raman and IR spectra of the complexes can be divided into three wavenumber regions, namely: 3500-3000 cm^{-1} (N-H and C-H stretching), 1700-400 cm^{-1} and below 400 cm^{-1}. The low frequency region is important for this study as the thallium – thiourea bands would be expected in this region if a formal covalent bond is formed between thallium and thiourea [6, 7].

3.3.1 THE REGION 3500 – 3000 cm^{-1} (Table 3.1)

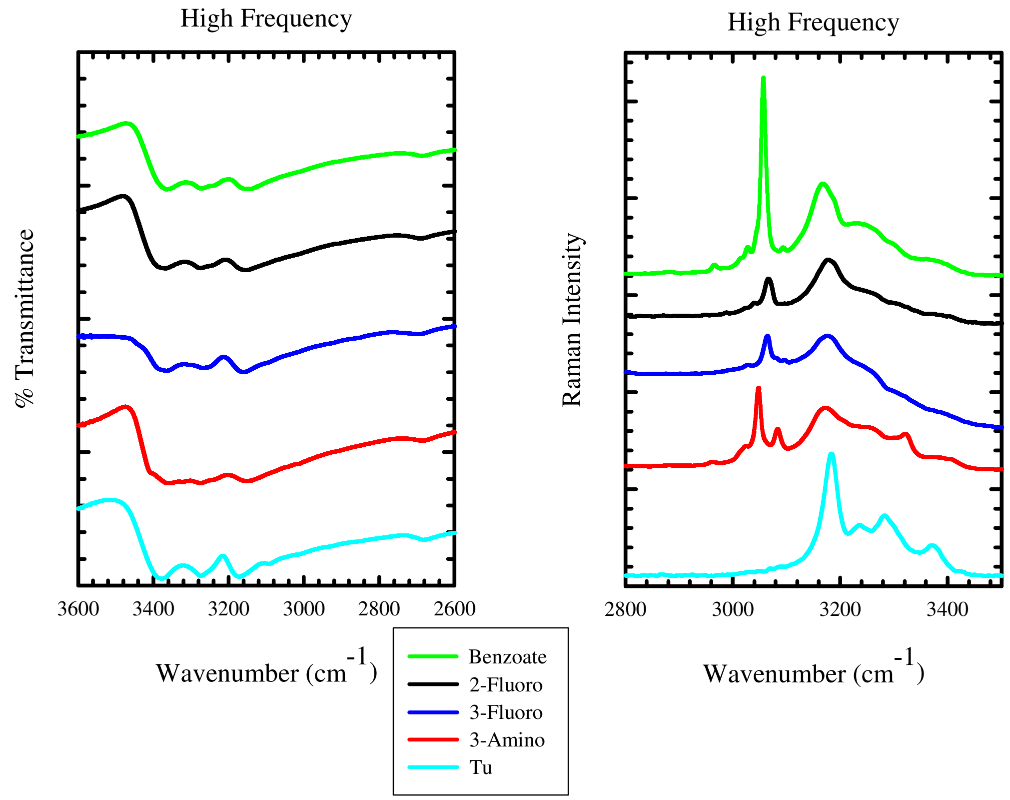

Fig. 3.3 **IR and Raman spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea in the region of 3500-3000 cm^{-1}**

This is an important region which contains the N-H stretch of the amine groups of thiourea and C-H stretch vibrations of the aromatic ring of benzoate ions [8]. The spectra are very similar and dominated by the bands originating from thiourea.

N-H region

It is generally agreed that the band in the thiourea spectrum at 3377 cm^{-1} is the antisymmetric stretch vibration, the peak at 3273 cm^{-1} represents the first overtone of the NH_2 antisymmetric bending component and the band at 3172 cm^{-1} represents N-H symmetric stretching [6, 9]. The spectrum of the 3-amino complex shows an extra band at 3323 cm^{-1} which can be attributed to the NH_2 group bonded to the benzoate ion [6, 8].

In both IR and Raman spectra there is a general shift to lower wavenumbers and broadening of the NH_2 vibrations which can best be observed in the Raman spectrum (Table 3.1 and Fig. 3.3). The shifting and broadening are indicative of an increase in hydrogen bonding in the complexes, compared to thiourea. This is in contrast to coordination metal – thiourea complexes, where a decrease in hydrogen bonding is observed (shift to higher wavenumbers). In these complexes a marked increase of intensity of the NH_2 bands is also observed and attributed to hydrogen bond weakening due to covalent metal – sulphur bonding that exists. The opposite is observed for the compounds of this study, indicative of the different bonding seen in these complexes..

As there are two different NH…..O approaches in the complexes a larger shift for the smaller approach value is expected as it is involved in stronger hydrogen bonding but the two hydrogen bonds were not resolved in the spectra.

C-H region

The C-H ring vibration is most clearly seen in the Raman spectra as a strong, sharp band between 3047-3083 cm^{-1} which is of course not seen in the pure thiourea spectrum, therefore must be attributed to the C-H vibrations of the ring [8, 10].

In the IR spectra these bands are less prominent as they are masked by the broad N-H band between 3143-3160 cm^{-1}.

THIOUREA		**BENZOATE COMPLEX**		**2-FLUORO COMPLEX**		**3-FLUORO COMPLEX**		**3-AMINO COMPLEX**		
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
3377ms	3370w	3365ms		3367ms		3365ms		3339w		1
								3323w	3321w	2
3273ms	3282w	3273ms		3275ms		3269ms		3274mw		3
			3231w							4
3172ms	3183ms	3143ms	3167m	3160ms	3177ms	3160ms	3175ms	3150m	3172m	5
					3066m		3064m		3083w	6
			3057ms						3047m	7

1 = N-H stretch/Ar-NH_2, 2-5 = N-H stretch, 6-7 = C-H stretch

Table 3.1 IR and Raman spectra wavenumbers for benzoate, 2-fluoro, 3-fluoro, 3-amino complexes and thiourea

3.3.2 THE REGION 1700 – 400 cm^{-1} (Table 3.3)

Within this region there are a number of bands present in both the IR and Raman spectra of the 3 complexes.

In terms of IR results, the thiourea band at 1617 cm^{-1}, which represents the NH_2 bending vibration overlaps with small weaker bands in the spectra of the 2-fluoro and 3-fluoro complexes. This is attributed to the aromatic C=C ring stretch of the complex which also occurs in this region. Thus it is difficult to determine exact assignments for these bands [6, 7, 9, 10]. The same main band is present in the spectra of the benzoate complex and the 3-amino complex, however, with little or no splitting. But due to the broadness of the band in both spectra the assignment may be NH_2 or C=C or both, as these bands may be masked. No prominent shifts in wavenumbers are seen relative to the thiourea.

The Raman spectrum of the thiourea shows a very weak band in the region at 1636 cm^{-1}, relating to the symmetric and antisymmetric-coupled bending mode $\delta(NH_2)$ [6, 7]. The strong NH_2 bands in the IR are absent and the assignment of the aromatic C=C stretch is unambiguous. The spectra of the 2-fluoro, 3-fluoro and the benzoate complexes all show a single sharp band at 1607 cm^{-1}, 1608 cm^{-1} and 1596 cm^{-1} respectively, which are attributed to the C=C stretch of the benzoate ion [10]. In the 3-amino complex spectrum this band occurs at 1603 cm^{-1}, however, it overlaps with the aromatic NH_2 which is also found in this region [8, 10].

The IR spectra of the 3-amino and benzoate complexes all possess a strong to medium band, 2-fluoro has a weak band and 3-fluoro has no band between 1550 - 1541 cm^{-1}. As this band is not seen in the thiourea spectrum, it is assigned to the COO^- of the benzoate ion, which occurs in this region [11, 12].

The Raman spectra shows very weak broad bands in this region which makes assignment difficult.

The IR spectra of thiourea and the 4 complexes (Fig. 3.5) show a band at 1473 cm^{-1} with a slight increasing shift visible in the Raman spectra (Fig. 2.6). This band is attributed to the antisymmetric (NCN) stretching of the thiourea [6, 7, 9].
At slightly lower wavenumbers (1450 cm^{-1}), the benzoate and amino complexes show medium to weak bands which can be assigned to ring vibrations as they are not present in thiourea spectrum [10, 13]. The strong IR band at 1413 cm^{-1} in pure

thiourea is also seen in the IR (Fig. 3.5) and Raman (Fig. 3.6) spectra of the three complexes and according to literature values can be assigned to the C=S vibration [8, 9].

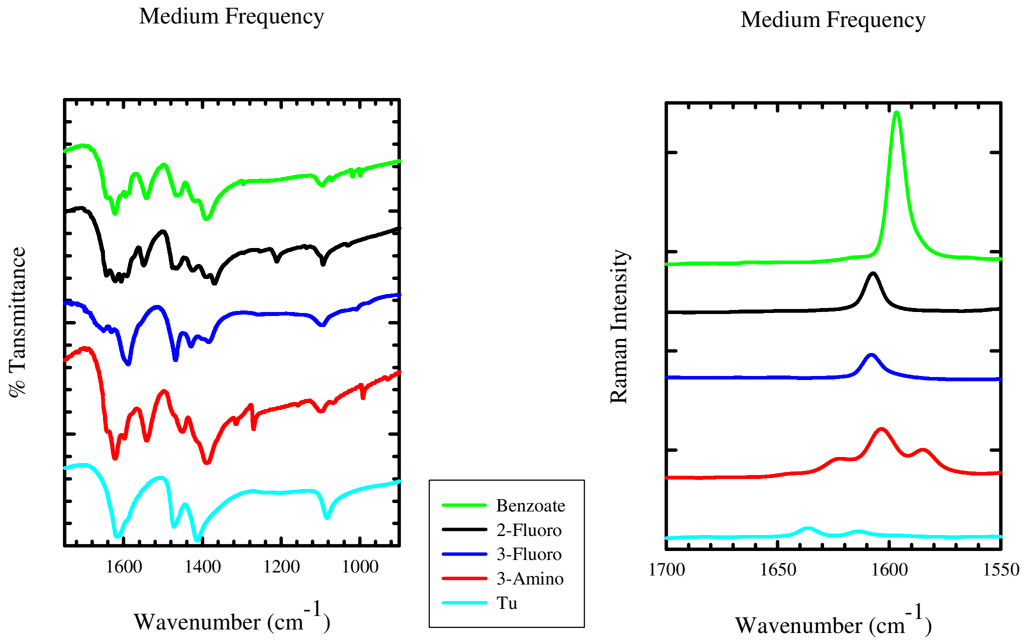

Fig. 3.4 **IR (region 1760 cm^{-1}-920 cm^{-1}) and Raman (region 1698 cm^{-1}-1554 cm^{-1}) spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea**

The Raman spectrum (Fig. 3.6) of thiourea shows a band at 1384 cm^{-1} with a shoulder at 1374 cm^{-1}. This band is present in the complexes as a single band with a shift to lower wavenumbers. It is assigned to a vibration that affects the whole thiourea molecule and has contributions from ν(CN), δ(NCN), δ(CNH) and ν(CS) [6, 7]. Note : ν = stretch δ = bend

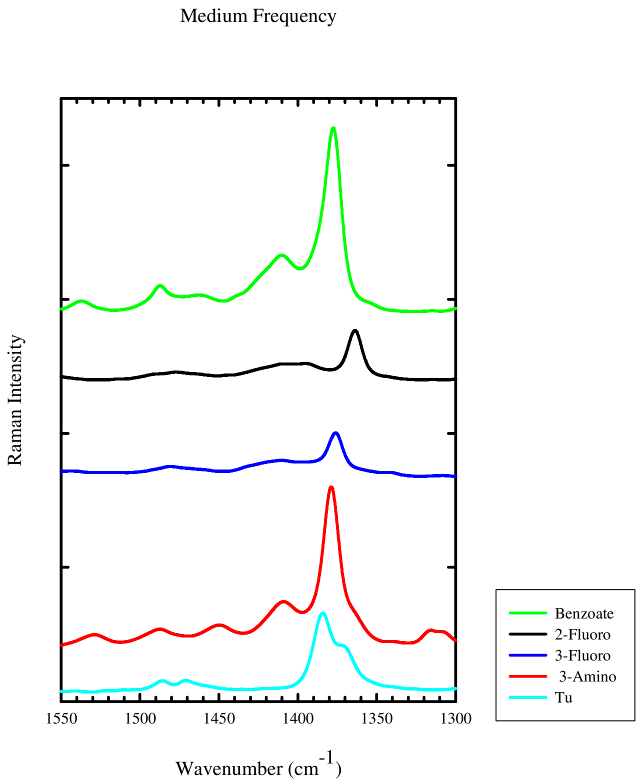

Fig. 3.5 **Raman (region 1550-1300 cm^{-1}) spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea**

Within the region of 1098-1083 cm^{-1} the bands are both IR and Raman active for both the thiourea and the 4 complexes.

Both the IR and Raman spectra of the complexes have a relatively strong band at approximately 1090 cm^{-1}. The Raman band at 1093 cm^{-1} in the thiourea arises from a mixed normal mode with contributions from ν(CN) and ρ(HNH) [6, 7, 8, 9, 10].

Between wavenumber values of 1030-486 cm^{-1} all the bands bar 3 are weak and correspond to C-H vibration of the aromatic ring [8, 10]. The first band of real importance is a strong band at 729 cm^{-1} and is present in both the Raman and IR spectra of both the thiourea and the 4 complexes. The band relates to a pure C=S stretch vibration of the thiourea and is relatively broad [5, 6, 8, 9, 14].

A large shift to lower wavenumbers is observed for the C=S stretch vibration of thiourea - metal coordination complexes where a coordination bond is formed between the metal and the sulphur atoms, as the double bond character of the C=S disappears upon coordination [6, 7]. No shift is observed for the complexes under investigation.

When discussing the C=S bond it is important to also take into consideration the interatomic distance between the metal and sulphur atoms. But it is also worth noting that because there are two different NH.....benzoic acid hydrogen bonds, this leads to two different S.....Tl interactions with in the complexes. The pairs of different S…..Tl distances observed for the four crystal structures determined in this study, as well as the results from the previously reported benzoate crystal structure [4], are given in Table 3.2.

COMPLEX	**Tl(1) – S(1)** **Å**	**Tl(1) – S(2)#1** **Å**
2-Fluoro #2	3.3792(7)	3.4235(8)
3-Fluoro #2	3.3537(7)	3.4142(8)
3-Amino #2	3.3588(6)	3.4209(7)
Benzoate #2	3.3642(7)	3.4345(9)
Benzoate #3	3.450	3.380

Table 3.2 Table showing the two different Tl – S interatomic distances

Note: #1 = Symmetry transformations used to generate equivalent atoms: x, y-1, z
#2 = This study
#3 = Ref. [4]

These complexes have Tl-S distances of similar magnitude. However, when one measures the Tl-S bond length in a coordination complex the bond length is only 2.45 Å (a considerable difference relative to the complexes in question) and which results in shifts up to 50 cm^{-1} in the spectra [6, 7]. As there are no shifts present in the complexes one is able to deduce that ionic interactions are dominant and little or no coordination character could be shown [15]. This is in accordance to the paper by Boeyens, on the crystal structure of the $C_6H_5COOTl{\cdot}4(SCN_2H_4)$, where it is stated that there is no formal Tl-S bond [16]. However, in a subsequent study of the chlorate complex, the Tl-S interatomic distances vary from 3.33 Å to 3.51 Å, and this is described as polymeric bonds [17]. In an earlier publication on ionic complexes of thiourea, it states that the average Tl-S distance 3.43 Å, which is considerably longer than the separation between sulphur atoms of coordinated ligands and metal atoms. As the sum of the thallium and sulphur atom radii is 2.70 Å and the sum of the ionic radii is 3.3 Å it is clear that the complexes are ionic and the main cohesive interactions are ion-dipole interactions [16].

The second band occurs in the IR of thiourea at 631 cm^{-1} and is of medium intensity. It is seen in the benzoate complex and is assignable to NCN [18].

The third band of importance is a large, prominent band in both IR and Raman spectra in the complexes at approximately 485 cm^{-1}. It is also present in the Raman and IR of thiourea at 479 cm^{-1} and 486 cm^{-1} respectively which corresponds to the published assignment [6, 8]. It usually shifts to lower wavenumbers upon coordination, but in our case shifts to higher wavenumbers with 10 cm^{-1}. This opposite shift could be indicative of the fundamental difference between covalent and ionic metal – thiourea complexes.

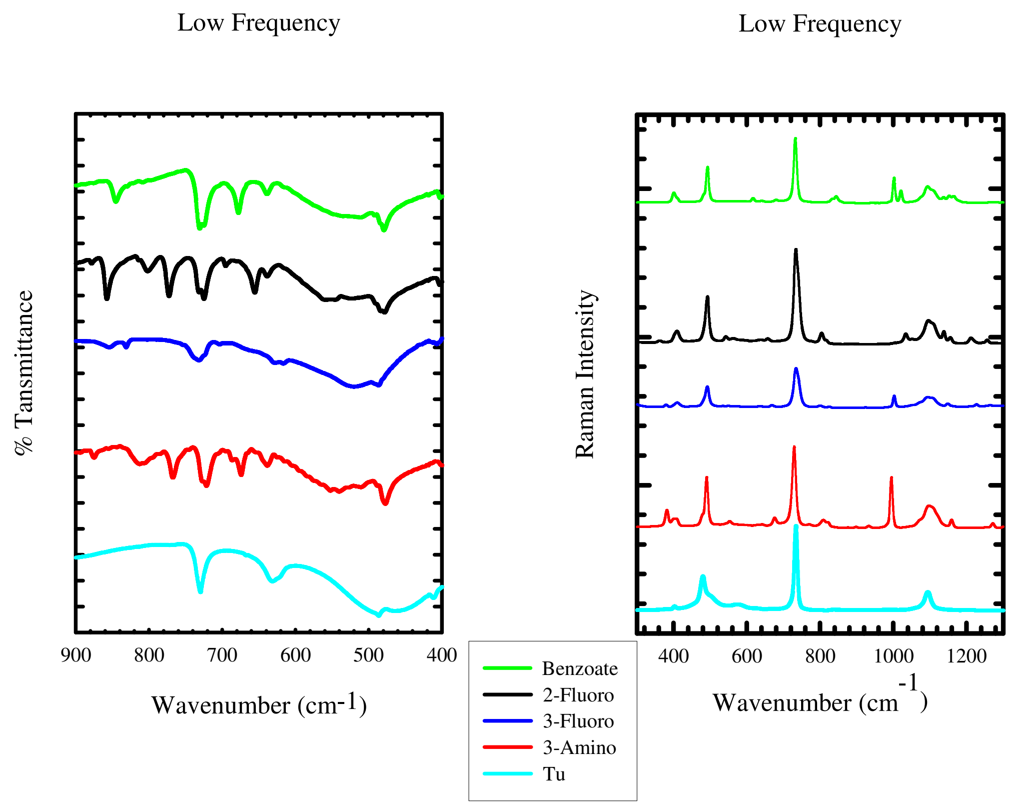

Fig 3.6 **IR (region 900 cm^{-1}-400 cm^{-1}) and Raman (region 1240 cm^{-1}- 320 cm^{-1}) spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea**

3.3.3 THE REGION 300 – 100 cm^{-1}

Only Raman spectra are available for this region and the metal – sulphur symmetric stretch bands expected to occur in this region (220 – 260 cm^{-1}) are not observed, which is supportive of the ionic nature of the complexes, which excludes the formation of a formal covalent bond between the thallium and sulphur atoms.

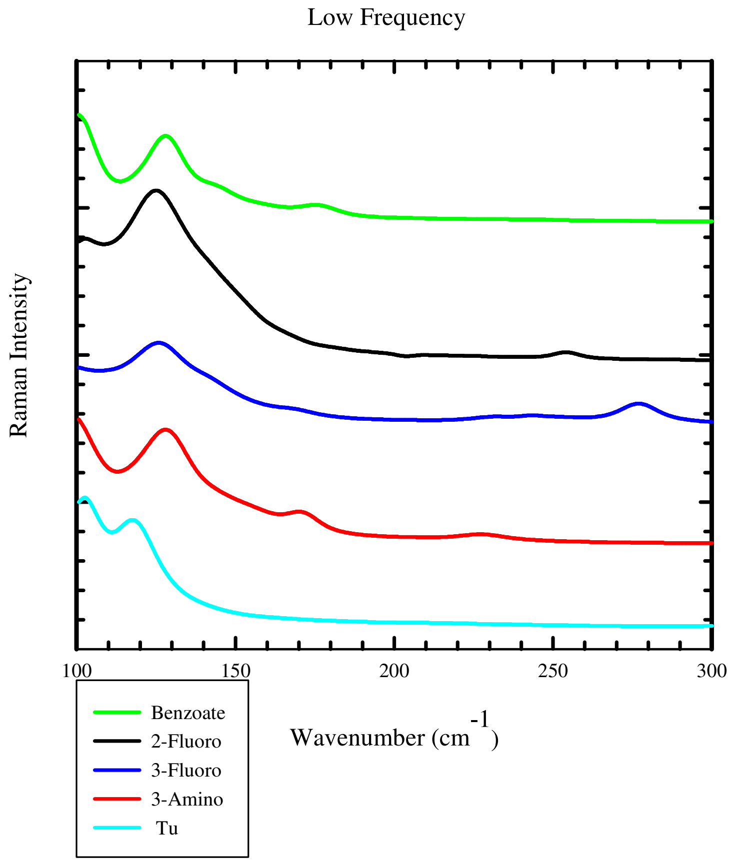

Fig. 3.7 **Raman (region 100-300 cm^{-1}) spectra of 2-fluoro, 3-fluoro, 3-amino, benzoate complexes and thiourea**

THIOUREA		**BENZOATE COMPLEX**		**2-FLUORO COMPLEX**		**3-FLUORO COMPLEX**		**3-AMINO COMPLEX**		
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
	1636w			1644w		1652w				1
1617s		1623s		1621w		1631w		1621s		2
		1596w	1596s	1597ms	1607m	1589s	1608w	1598w	1603m	3
		1542m	1537w	1550w	1550w			1541ms	1528w	4
1473ms	1471w		1487w	1469m	1477w	1468s	1481w		1487w	5
		1457m						1450mw	1449w	6
1413s			1410w	1427mw	1395w	1429mw	1410w		1409w	7
	1384m	1390s	1377s	1370m	1365ms	1384mw	1376m	1388s	1378s	8
1083s	1093ms	1098mw	1093ms	1094m	1095ms	1096m	1093s	1098mw	1096ms	9
			1020m		1030w					10
			1001ms				1002ms	992w	994s	11
		845w	843mw	858mw		855w				12
				801w	803w			809mw		13
				773w				767m		14
729m	734s	731ms	732s	731m	733s	732m	734s	721m	729s	15
		678mw						674mw		16
631m		639w								17
			616w			617w				18
	573w									19
486ms	479s	479m	492s	484m	492s	486s	491s	477ms	490s	20

1-2 = NH_2, 3 = NH_2/C=C/Ar-NH_2, 4 = COO^-, 5 = NCN/C=C, 6 = C=C, 7-8 = C=S, 9 = NH_2/C=S/C-N/C-H, 10-14 = C-H, 15 = C=S, 16 = NH_2/C=S/NCN, 18-19 = C-H, 20 = NCN/C=S

Table 3.3 **IR and Raman wavenumbers for benzoate, 2-fluoro, 3-fluoro, 3-amino complexes and thiourea**

3.4 RAMAN AND IR SPECTRA OF THE OTHER 17 COMPLEXES

IR and Raman spectra for the full list of complexes that was synthesised were obtained. The main bands were all very similar in all the spectra as can be seen from the tables in 3.6. The detailed analysis confirmed the same increase in hydrogen bonding as observed for the previous four samples (similar shifts in thiourea bands), as well as the ionic nature of the metal – sulphur band. Thus, it was concluded that the solid state structures of all complexes are in fact quite similar. The bands that are expected to be different are discussed below.

Ar-NO_2 Delocalized NO_2 stretching vibrations seen at1338 cm^{-1}. The vibrations do not correspond exactly to literature values as substituted nitrobenzenes are affected by inductive effects,

	resonance effects and hydrogen bond formation related to the benzene ring substituents [8].
HALOGENS	The complexes which contain halogen substitution, i.e. 2/3/4-fluoro, 2/3/4-bromo, 2/3/4-chloro complexes do not show well defined C-X (X = halogen) absorptions as halogen substituted aromatics result in absorptions that occur in a spectral region that is crowded by other important group frequencies [10].
2/3/4-METHYL 4-METHOXY 2-HYDROXY	All are difficult to identify due to overlapping of other important bands in the region they occur.

As has been stated in chapter one, all the complexes were initially synthesised and analysed with $TlNO_3$ as the starting material before being resynthesised with Tl_2CO_3 and reanalysed. Due to the presence of NO_3 in some of the complexes in the first batch, there was an uncertainty in the infrared band assignment at 1384 cm^{-1} as TU and NO_3 overlap. In the second batch with no NO_3 or CO_3 it can be seen that the band in question relates to TU, specifically C=S.

Note : Proof of no CO_3 contamination is assured. The complete absence of the characteristic CO_3 band at 1039 cm^{-1} from all the complex IR spectra proved that there was no carbonate present in any of these samples.

3.5 CONCLUSION

The FT-Raman and FT-IR bands in the spectra of all the complexes have been assigned according to literature data. The complexity of the spectra, which contain bands originating from the anions, as well as thiourea, makes some of the assignments ambiguous as indicated in the tables and figures.

Some important conclusions could be drawn from the spectra.

- An increase in hydrogen bonding, reflected by the observed changes relative to the thiourea spectra, is observed for all the complexes measured. The presence of hydrogen bonding indicated broadening and shifting to lower wavenumbers in the IR and Raman spectra. This is also supported by the observation that two different hydrogen bonds were observed in the single crystal study of the four benzoate structures. It was however not possible to distinguish between the two bonds of 2.92 Å and 3.03 Å.
- The absence of a band due to covalently bonded Tl-S is in accordance with the ionic nature of the complexes. The Tl-S distances as measured in the crystallographic study also supports the observation from this spectroscopic study that thallium is not covalently bonded to sulphur and the ionic model as suggested in references [16, 17] is correct.

3.6 IR AND RAMAN BANDS FOR ALL THE COMPLEXES

The following complexes did not give Raman spectra of sufficient quality for interpretation bar the one band at approximately 733 cm^{-1} which is characteristic of C=S : 2-bromo, 2-hydroxy, 3-nitro, 4-fluoro,2/3/4-chloro

2-AMINO COMPLEX		3-AMINO COMPLEX		4-AMINO COMPLEX		ASSIGNMENT
IR	RAMAN	IR	RAMAN	IR	RAMAN	
3376ms		3339w		3368m		N-H stretch
		3323w	3321w			N-H stretch
3276ms		3274mw		3275m		N-H stretch
3164s	3185ms	3150m	3172mw	3171m	3184m	N-H stretch
			3083w			C-H stretch
			3047mw			C-H stretch
1598s	1607w	1621ms	1603m	1599ms	1607w	Ar-NH$_2$/C=C/NH$_2$
		1598w				NH2/C=C/Ar-NH2
		1541ms	1528w			COO$^-$
1469ms	1474w		1487w	1469mw	1474w	C=C/NCN
		1450mw	1449w			C=C
1433w			1409w	1433w		C=S
1384w	1393w	1388s	1378ms	1383w	1394w	NH$_2$/C=S/NCN
1094mw	1106m	1098w	1096ms	1095m	1105m	NH$_2$/C=S/C-N/C-H
		992w	994s			C-H
853w		809mw		850ms		C-H
		767mw				C-H
732m	740s	721mw	729s	730s	740s	C=S
		674mw				C-H
486s	493s	477s	490s	483s	492s	NCN/C=S

Table 3.4 IR and Raman wavenumbers for 2/3/4-amino complexes

2-NITRO COMPLEX		3-NITRO COMPLEX		4-NITRO COMPLEX		ASSIGNMENT
IR	RAMAN	IR	RAMAN	IR	RAMAN	
3338w		3366w		3368m		N-H stretch
3289m		3279m		3279m		N-H stretch
3161ms	3183ms	3161ms		3163ms	3184m	N-H stretch
					3076w	C-H stretch
1600s	1606w	1599s		1599s	1594ms	NH$_2$ /C=C
1471ms	1476w	1470m		1470ms		C=C/NCN
1428w		1429w		1432w		C=S
1385ms	1398w	1383m		1385mw	1387m	NH$_2$/C=S/NCN
	1336w				1338m	Ar-NO$_2$
1092ms	1106m	1097m		1094m	1106m	NH$_2$/C=S/C-N/C-H
	1050w					C-H
861m				853w		C-H
				801mw		C-H
730ms	740s	725ms		732m	740s	C=S
484ms	493ms	487m		487m	492ms	NCN/C=S

Table 3.5 IR and Raman wavenumbers for 2/3/4-nitro complexes

2-FLUORO COMPLEX		**3-FLUORO COMPLEX**		**4-FLUORO COMPLEX**		**ASSIGNMENT**
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
3367ms		3365ms		3367ms		N-H stretch
3275ms		3269ms		3273ms		N-H stretch
3160ms	3177ms	3160ms	3175ms	3162ms		N-H stretch
	3066m		3064m			C-H stretch
1644w		1652w				NH2
1621w		1631w				NH2
1597ms	1607m	1589s	1608w	1602s		NH$_2$/C=C
1550w	1550w			1553mw		COO$^-$
1469m		1468ms		1469m		C=C/NCN
1427mw	1395w	1429mw		1431mw		C=S
1370m	1365ms	1384ms	1376w	1387s		C=S
1094m	1095ms	1096m	1093m	1084mw		NH2/C=S/CN/C-H
	1030w		1002mw			C-H
858mw		855w		856mw		C-H
801w						C-H
773w				782w		C-H
731m	733s	732m	733s	733mw		C=S
		617w				C-H
484m	492s	486s	491s	486m		NCN/C=S

Table 3.6 **IR and Raman wavenumbers for 2/3/4-fluoro complexes**

2-BROMO COMPLEX		**3-BROMO COMPLEX**		**4-BROMO COMPLEX**		**ASSIGNMENT**
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
3366ms		3367ms		3360ms		N-H stretch
3277ms		3267ms		3259ms		N-H stretch
3162s		3157ms	3169m	3159s	3174m	N-H stretch
			3078mw		3088ms	C-H stretch
			3048m		3071ms	C-H stretch
		1622m				C=C/NH$_2$
1599s		1601mw	1587ms	1587s	1586ms	NH$_2$/C=C
		1543ms	1535w	1543m		COO$^-$
1470ms		1467ms	1464w	1466m	1480w	NCN/C=C
1429mw				1429mw		C=S
			1405w	1404m		C=S
1387mw		1371s	1366s	1384s	1372s	NH$_2$/C=S/NCN
1097mw		1096mw	1091s	1093w	1108mw	NH$_2$/C=S/C-H/CN
				1074w	1071s	C-H
			999s		1014w	C-H
855w		858mw	858w	838w		C-H
			830w		837mw	C-H
		768mw		770mw		C-H
730m		724m	732s	729mw	731s	C=S
			650mw			C-H
488m		489ms	489s	486ms	485s	NCN/C=S

Table 3.7 **IR and Raman wavenumbers for 2/3/4-bromo complexes**

2-CHLORO COMPLEX		**3-CHLORO COMPLEX**		**4-CHLORO COMPLEX**		**ASSIGNMENT**
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
3367ms		3367ms		3359m		N-H stretch
3270ms		3274ms		3253m		N-H stretch
3162ms		3162ms		3157m		N-H stretch
1594s		1600m		1589s		NH_2/C=C
		1545m		1545m		COO^-
1468ms		1468m		1467m		C=C/NCN
1430mw				1428w		C=S
1384mw		1375ms		1386s		NH_2/C=S/NCN
1094mw		1098w		1099m		NH_2/C=S/CN/C-H
				1012w		C-H
		869w				C-H
				839w		C-H
		769mw		774m		C-H
732m		738m		729m		C=S
487s		479m		485w		NCN/C=S

Table 3.8 **IR wavenumbers for 2/3/4-chloro complexes**

2-METHYL COMPLEX		**3-METHYL COMPLEX**		**4-METHYL COMPLEX**		**ASSIGNMENT**
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
3366ms		3366ms		3366ms		N-H stretch
3276ms		3274ms		3278ms		N-H stretch
3161ms	3185ms	3159ms	3179ms	3161ms	3184ms	N-H stretch
			3042w			C-H stretch
1598s	1607w	1599s	1602w	1598s	1607w	NH_2/C=C
1472m		1469m		1470m		C=C/NCN
1430w				1431w		C=S
1383w	1393w	1383s	1386w	1382w	1393w	NH_2/C=S/NCN
1093m	1106m	1098m	1106m	1093ms	1106m	NH_2/C=S/CN/C-H
			1005mw			C-H
854mw				852m		C-H
733m	740s	731ms	737s	730m	740s	C=S
485m	493s	490m	490s	483m	493m	NCN/C=S

Table 3.9 **IR and Raman wavenumbers for 2/3/4-methyl complexes**

4-METHOXY COMPLEX		**2-HYDROXY COMPLEX**		**BENZOATE COMPLEX**		**ASSIGNMENT**
IR	**RAMAN**	**IR**	**RAMAN**	**IR**	**RAMAN**	
3369ms		3366ms		3365m		N-H stretch
3277ms		3268ms		3273ms		N-H stretch
					3231w	N-H stretch
3164s	3185ms	3158s		3143ms	3167m	N-H stretch
					3057ms	C-H stretch
				1623s		NH_2
1599s	1607w	1589s		1596w	1596s	NH_2/C=C
				1542m	1537w	COO^-
1470m	1475w	1468m		1457m	1487w	C=C/NCN
1433w		1430w			1410w	C=S
1383w	1389w	1382m		1390s	1377s	NH_2/C=S/NCN
1093m	1106m	1093mw		1098mw	1093ms	NH_2/C=S/CN/C-H
					1020m	C-H
					1001ms	C-H
853mw		862w		845w	843mw	C-H
733m	740s	730mw		731ms	732s	C=S
				678mw		C-H
				639w		NH_2/C=S/NCN
					616w	C-H
486m	493s	486m		479m	492s	NCN/C=S

Table 3.10 **IR and Raman wavenumbers for 4-methoxy, 2-hydroxy, benzoate complexes**

3.7 REFERENCES
CHAPTER 3

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