# Structural studies of thallium(I)-thiourea complexes

by

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# SUMMARY

**Structural Studies of Thallium(1)-Thiourea Complexes**

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It is known that from research carried out in 1968 by L.H.W. Verhoef and J.C.A. Boeyens that the combination of thallium(1) salts, thiourea and benzoic acid results in the formation of ( $Tl^{+}.4TU$ )$_n$ coordination columns ( TU = Thiourea ) with the benzoate ions also positioning themselves in linear stacks or columns [1].

Various complexes were synthesised from $Tl_2CO_3$ with different benzoic acid derivatives and thiourea in order to observe the effects this may have on the Tl(1)-thiourea complexes. It was also possible to confirm the formation of the intermediate product [Tl $(OC(O)C_6H_4)R$], R = 4-$NH_2$, by single crystal analysis.

The benzoic acid derivatives incorporated a wide range of both electron withdrawing and electron donating substituent groups at the ortho, meta and para positions. Also included for completeness were bulky group substituents.

[$NH_2$, $NO_2$, $CH_3$, Cl, F, Br]$_{ortho,\ meta\ and\ para}$, 4-methoxy, and 2-hydroxy benzoic acid derivatives were the specific substituents included in this study. The only benzoic acid derivative complexes which yielded diffraction quality crystals suitable for single crystal studies were the 2-fluoro, 3-fluoro, 3-amino and benzoate complexes. The crystal structures for the complexes with $PF_6^-$ and $BF_4^-$ as anions were also determined as well as that of 2Tl(I), 2(TU) 2(Tph) $2H_2O$ (Tph = terephthalate benzene-1,4-dicarboxylate) complex.

All benzoic acid derivative complexes were analysed using x-ray powder diffraction. The powder diffraction data of all benzoate complexes could be split into five different groupings of complexes with similar patterns. One such group contained

the four isostructural complexes. Another group had eight complexes with only 2- and 4-substituted benzoates present.

The results of the x-ray powder and single crystal diffraction studies prove beyond doubt that the four benzoic acid derivative complexes are isostructural. Thus changing the substituent on the aromatic ring in the anion plays little or no role in the size or shape of the cavity/channel that forms with in the complex.

Spectroscopic studies ( IR, Raman, UV, NMR ) as well as thermal and mass spectroscopy studies were carried out on all the complexes as a means of identification and proof of complexation, as well as to study the molecular interactions in the solid state.

As a result of this and the similarity of the IR/Raman, UV and thermal studies of these four complexes to the other synthesised complexes, one can say that all the complexes that were prepared have indeed very similar solid state interactions.

The thermal studies reflected the effects of changing the electronic character of the substituent on the benzoate. Also, the thermal behaviour of the thiourea molecules in the the complexes was analysed.

Reference: [1] L. H. W. Verhoef and J. C. A. Boeyens, Acta Cryst. 1969. **B25**, 607