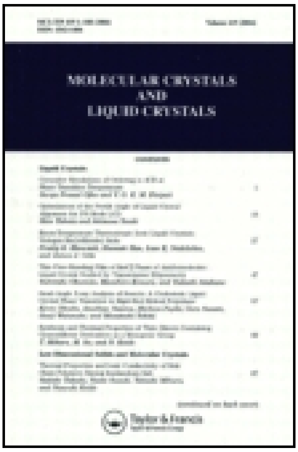

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# Inclusion of a Protonated Amine in Thiourea-Chloride and -Bromide Matrix. Expected Ionic Conducting Materials

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# Inclusion of a Protonated Amine in Thiourea-Chloride and -Bromide Matrix. Expected Ionic Conducting Materials

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The reaction of thiourea with 1-azabicyclo[2,2,2]octane (quinuclidine) and quinuclidine hydrochloride or quinuclidine hydrobromide in ethanol/acetone mixture leads to the formation of the inclusion compounds $(\text{thiourea})_2[(\text{quinuclidine})_2H]^+Cl^-$ and $(\text{thiourea})_2[(\text{quinuclidine})_2H]^+Br^-$, respectively. The crystal structure of the ternary proton-amine-thiourea complex may be described as the inclusion of the hydrogen-diquinuclidine cationic complex in a stacked form in the van der Waals cavities of a polyanionic thiourea-chloride and –bromide superstructure.

Complete structure determination of the products was performed and show channel structure formed by monodimensional, non intersecting polimeric chains of thiourea molecules linked by chloride or bromide ions.

**Keywords**

inclusion compounds; thiourea; quinuclidine; supramolecular.

## INTRODUCTION

Urea and thiourea are known to form numerous crystalline "host-guest" inclusion compounds. In these products, the urea or thiourea molecules form extensive hydrogen bond host structures in which a variety of guests molecules of appropriate size and shape are included[1-4]. The nature of both the vacancies in the amidic host and the host-guest interactions, as well as the "self assembling" capability of the system may be considered as a model for biological system, especially for features occurring in cavities inside protein structures. From this point of view, it is interesting to investigate the conditions determining this type of molecular self organisation. Thiourea frequently forms macromolecular complexes displaying stoichiometries with host-guest ratios of 1:3n where n, which is approximately an integer, depends on the size of the guest. In these conventional inclusion compounds , thiourea molecules are arranged in Hydrogen bonding networks which define one-dimensional, non interacting tunnels[5-7]. This is indeed the most stable configuration for products arising from the inclusion of inert host molecules as hyrocarbons or some mono-functional amines[8], in the thiourea matrix. In this work we show the formation of a new extended thiourea matrix derivative. The interest of this study is obtain new materials with probably anisotropy conducting properties.

This inclusion phenomena in this special thiourea matrix may be of great interest for modelling of biological systems as well as the mobility of the guest cationic species expected for this kind of host-guest complex may be useful for developing new conducting materials.

## EXPERIMENTAL

Commercially available thiourea (Merck), quinuclidine (Aldrich) and LiCl or LiBr (Aldrich) .were used as received. The products were prepared by mixing at room temperature the thiourea, the amine and the lithium salt in methanol solution in the stoichiometric ratio 2:1:1. Slow solvent evaporation leads to large prismatic shape crystals which were collected, washed with cold methanol, and dried under vacuum. The colourless crystalline products have the composition $[Q_2H]^+[Tu_2Cl]^-$

(Found (calc.): C, 46.5 (46.7); N, 20.2 (20.4); S, 14.6 (15.6); H, 8.7 (8.6)%) and $[Q_2H]^+[Tu_2Br]^-$ (Found (calc.): C, 41.9 (42.1); N, 18.3 (18.5); S, 13.3 (14.1); H, 7.9 (7.8)%).

A single crystal was selected for the X-ray diffraction analysis. Data were collected on a Siemens R3m/V diffractometer with graphite monochromated MoKα radiation (λ= 0.71073 Å) at 293 K.

DTA and TG were performed in an STA 409 NETZSCH equipment, with 5°C per minute heat velocity in the range room temperature at 450°C in nitrogen atmosphere.

## RESULTS AND CONCLUSIONS

The thiourea-quinuclidine.HCl and thiourea-quinuclidene.HBr host-guest complex may be described as a helicoidal hexagonal-chanel structure in which thiourea networks are held together by protonated quinuclidine bridges. In Figure 1 are illustrated the structure of the new thiourea derivative matrix.

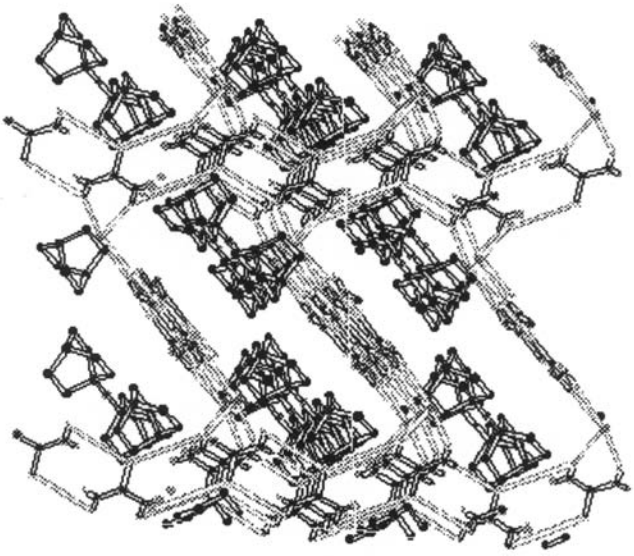

**FIGURE 1.** Channel nature of the supramolecular structure of the compound $[Q_2H]^+[TU_2BR]^-$

The differential termic analysis of the ternary inclusion compounds and thiourea are compared between 30 and 400°C. That show three endothermic process like is observed in the Figure 2, different to the quinuclidina that presents only one endothermic peak around of 119°C..

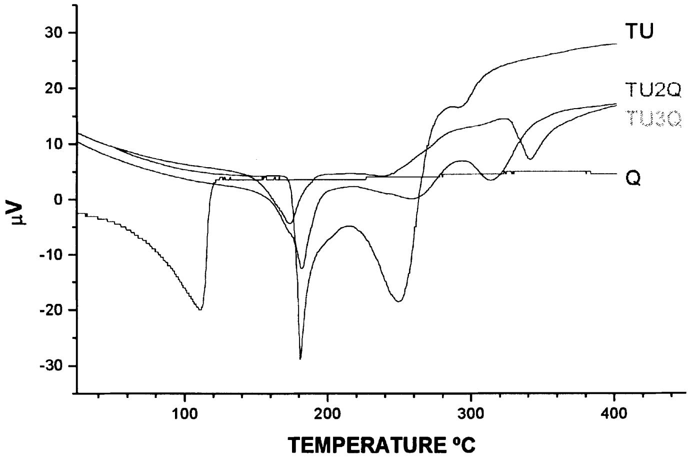

**FIGURE 2.** DTA comparison between thiourea, quinuclidina and the inclusion compounds $[Q_2H]^+[TU_2CL]^-$ AND $[Q_2H]^+[TU_2BR]^-$

The termogravimetric analysis of the synthesised compounds show variations of the mass loss in relation with the pure thiourea, and very different to the pure quinuclidine, however, are similar with the other inclusion compounds. That is observed in the Figure 3 and Table 1.

**TABLE 1.** Mass loss of the inclusion compounds in different step of thermal decomposition

| Mass loss in % | TU2Q | TU3Q |
|---|---|---|
| 1st | 17.59 | 16.82 |
| 2nd | 30.94 | 41.57 |
| 3th | 39.96 | 51.26 |

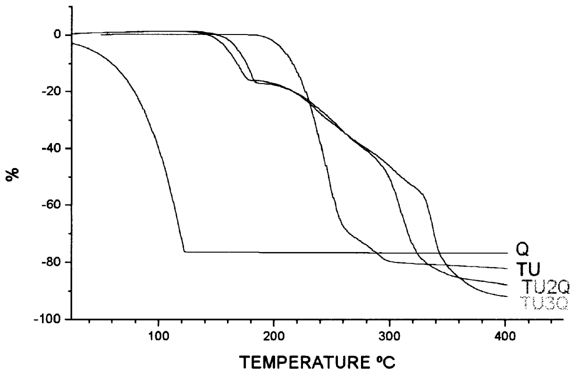

**FIGURE 3.** Mass loss of thiourea, quinuclidine and inclusion compounds with increase of temperature

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