

Synthesis, Microhardness, FT-IR, and Thermal Decomposition of Semiorganic Antimony Thiourea Bromide Monohydrate Single Crystals

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Abstract Antimony thiourea bromide monohydrate (ATBM) single crystals were grown by a solution growth technique at room temperature. Microhardness studies on the grown crystal were carried out using the Vickers microhardness tester to estimate the mechanical strength of the crystal. The FT-IR analysis ascertains the presence of a metal–sulphur bond in ATBM crystals. The thermal decomposition of ATBM crystals was investigated by means of thermogravimetric analysis.

Keywords FT-IR spectrum · Microhardness · Semiorganic · TGA/DTA · Thermal decomposition

1 Introduction

Single crystals of some inorganic complexes of thiourea are gaining importance in recent years because of their unique optical properties [1–3]. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment [4] and its ability to form an extensive network of hydrogen bonds. In addition, the complexes of some main group elements [5], such as antimony, can possess a certain biological function like contributing for the clearance of the parasitic infection Leishmaniasis [6–8]. To synthesize complexes of antimony will be interesting not only for main group element chemistry, but also bioinorganic chemistry [9].

In the work of growing semiorganic crystals of antimony thiourea bromide monohydrate (ATBM), thiourea which is a typical polar molecule, was selected to combine with antimony bromide. Bhat and Dharmaprakash [10] have grown single crystals of ATBM in sodium meta silicate gel at ambient temperature. Upadhya and Udayashankar [11]

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have grown single crystals of ATBM which has the molecular formula $\text{Sb}[\text{CS}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{O}$ by a solution growth technique at room temperature and studied its structure by X-ray single crystal diffraction. Karthick et al. [12] grew single crystals of Bis thiourea antimony tri bromide (BTAB) from aqueous solution by a slow cooling technique and studied their structural, thermal, mechanical, linear, and nonlinear optical properties. In the present investigation we report the growth of ATBM single crystals by a solution growth technique, their microhardness, infrared spectrum, and thermal decomposition.

2 Experimental

For 100 mL concentrated hydrobromic acid (HBr, Merck, purity 47 %), 7 g of antimony oxide (Sb_2O_3 , Merck, purity 99.5 %) were mixed, stirred well, and filtered to get an antimony bromide solution. This solution is thoroughly mixed with 14 g of thiourea [$\text{CS}(\text{NH}_2)_2$, Merck, purity 99 %] dissolved in 300 mL of distilled water, filtered, and kept at room temperature. Good quality yellow colored ATBM crystals were obtained after a period of five days. The MERCURY 2.2 drawing of the asymmetric unit of this compound with atom labeling is shown in Fig. 1. Vickers microhardness, infrared spectra, and thermal studies for this crystal were performed by using instrumental methods and are presented in detail in the following section.

3 Results and Discussion

3.1 Vickers Microhardness Test

The grown ATBM crystal polished with *N,N*-dimethylformamide was subjected to microhardness studies using a digital microhardness tester MMT-X7. The static

Fig. 1 Asymmetric unit of $\text{Sb}[\text{CS}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{O}$. Thermal ellipsoids are shown at 50 % probability

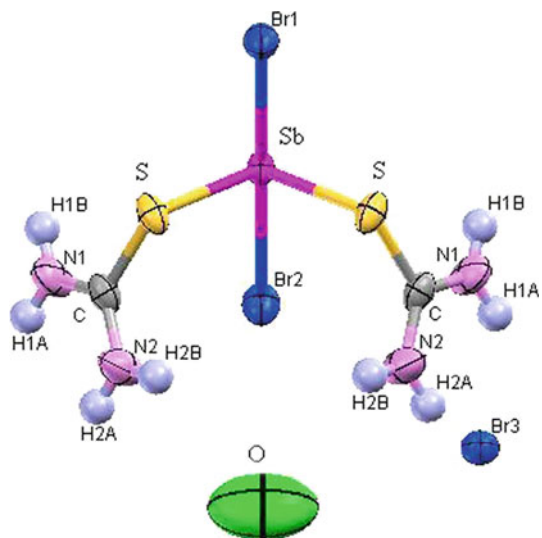
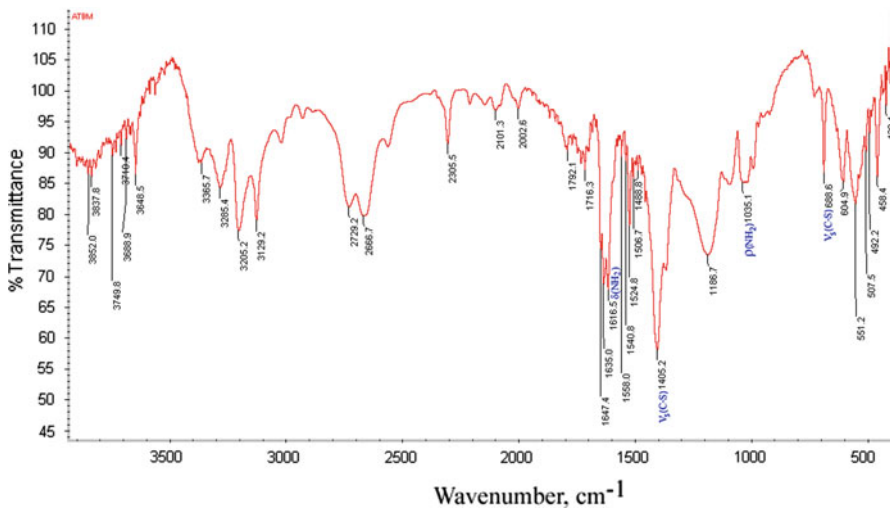


Table 1 Vickers microhardness number (HV) of grown ATBM for the ($\bar{1}10$) plane

Load (g)	HV	Diagonal X	Diagonal Y
5	47	14.3	13.9
10	46	20.7	19.6
25	46	31.1	32.1

**Fig. 2** FT-IR spectrum of ATBM crystal using KBr pellet technique

indentations were made at room temperature with a constant indentation time of 10 s for all indentations. The indentation marks were made on the ($\bar{1}10$) face of the crystal by varying the load. The development of a crack in the crystal surface by indentation at 25 g due to the release of internal stresses generated locally made the indentation to be restricted to 25 g. The Vickers microhardness number has been calculated using $HV = 1.8544P/d^2 \text{ kg} \cdot \text{mm}^{-2}$ where P is the applied load, d is the mean diagonal length of the indenter impression, and 1.8544 is a constant, a geometrical factor for the diamond pyramid. Since the indenter gives geometrically similar indentations, the measured hardness must be independent of the applied load [13]. The Vickers microhardness number (HV) of grown ATBM for the ($\bar{1}10$) plane is given in Table 1. The softer the crystal, the more mobile would be the dislocations resulting in the crystal, showing a higher tendency to strain-harden [14].

3.2 FT-IR Analysis

The FT-IR spectrum of grown ATBM crystals was recorded with a Nicolet Avatar 330 FT-IR spectrometer in the wavelength range of 500 cm^{-1} to 4000 cm^{-1} by a KBr pellet technique. The spectrum is shown in Fig. 2. A few peaks were found to be shifted slightly when compared with the spectrum of thiourea [15, 16] due to the following reason. The structure of ATBM reveals that antimony bonds with sulphur

Table 2 Assignment of IR band frequencies in ATBM crystal and decomposition product

Thiourea (cm^{-1})	ATBM (cm^{-1})	Decomposition product after heating at 292 °C (cm^{-1})	Assignments ^a
3375	3365.7		$\nu(\text{N-H})$
3280	3285.4		$\nu(\text{N-H})$
1618	1616.5	1607.3	$\delta(\text{NH}_2)$
1471	1524.8		$\nu_{\text{as}}(\text{C-N})$
1412	1405.2	1400.1	$\nu_{\text{s}}(\text{C-S})$
1086	1035.1	1088.3	$\rho(\text{NH}_2)$
730	688.6		$\nu_{\text{s}}(\text{C-S})$

^a δ Deformation, ν band stretching, ρ rocking, s symmetric, as asymmetric

Table 3 Comparison of H₂O mode vibrations in ATBM crystal with isolated water molecule [17]

Isolated water molecule (cm^{-1})	ATBM (cm^{-1})	Decomposition product after heating at 292 °C (cm^{-1})	Assignments ^a
500–800	458.4	468.1	Wagging of H ₂ O (ν_{L})
	551.2	553.0	Rocking H ₂ O (ν_{L})
	604.9	600.0	
1643.5	1635.0		$\nu_2\text{H}_2\text{O}$
2127.5	2101.3		Combination of ($\nu_{\text{L}} + \nu_2$)H ₂ O
3404	3648.5		ν_1 and ν_3 H ₂ O

^a ν_{L} Librations, ν_1 symmetrical stretching vibrations, ν_3 asymmetrical stretching vibrations, ν_2 bending vibration

[11], as most of the metals form complexes via sulphur [17]. Hence, the C–S stretching frequency should decrease and that of C–N should increase on complex formation [17]. The absorption at 1618 cm^{-1} due to the NH₂ deformation mode is not affected indicating the absence of a nitrogen metal bond. Absorption at 1086 cm^{-1} due to the NH₂ rocking mode is not affected by the formation of the metal–sulphur bond alone. Thus, the metal–sulphur bond is assumed to be responsible for the shifting of the vibration at 1412 cm^{-1} and 730 cm^{-1} to a lower frequency [17]. A comparison of vibrations of thiourea with the grown ATBM crystal is shown in Table 2.

Librational modes, viz., rocking, twisting, and wagging modes of the water molecule can be expected in the 500 cm^{-1} to 800 cm^{-1} region [18–20]. The appearance of stretching modes at wave numbers higher than those of a free water molecule and the bending mode at a lower wave number confirm that water of crystallization is weakly bonded in ATBM [19] which is in agreement with the structural analysis [11]. A comparison of H₂O mode vibrations in the grown ATBM crystal with an isolated water molecule is shown in Table 3.

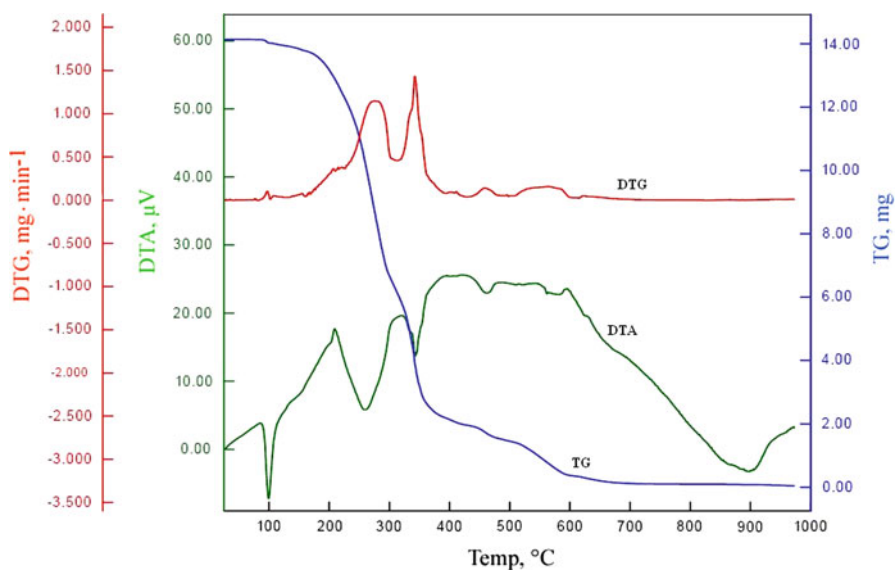


Fig. 3 TGA and DTA thermogram of ATBM crystal in nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$

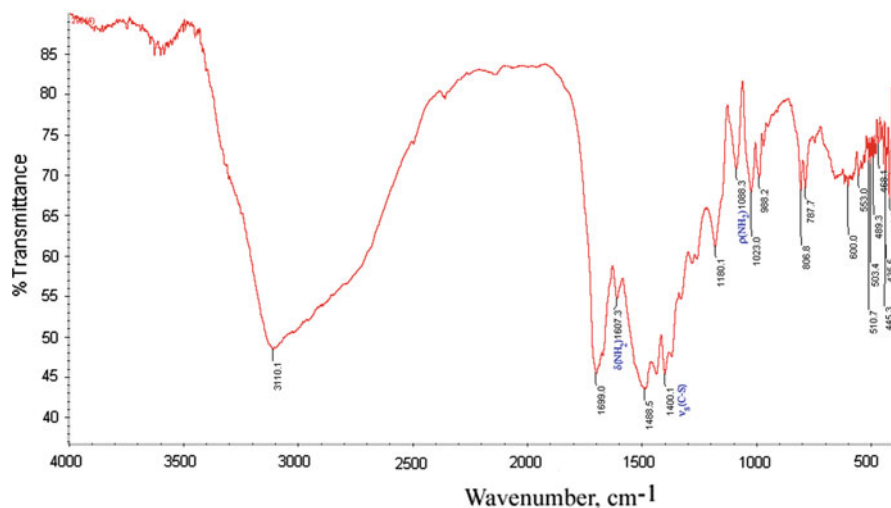
3.3 Thermal Studies

The TG/DTA analysis of dried powder of single crystals of ATBM was carried out in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ using a thermogravimetric/differential thermal analyzer EXSTAR6000 TG/DTA 6300. A horizontal differential type balance method was employed here. The TGA and DTA thermogram of ATBM is shown in Fig. 3. The crystal is stable up to 94°C and thereafter it begins to melt. During the process from 94.4°C to 184.7°C , it loses mass due to the loss of water of crystallization and corresponds to an endothermic peak at 100.6°C . Here the experimental mass loss (4.0 %) is very close to the theoretical value (3.4 %) and no phase transformation is observed.

From 184.7°C to 291.5°C , the mass loss is due to the loss of Br_2 and $\text{SC}(\text{NH}_2)_2$ from the complex corresponding to an endothermic peak at 264.7°C . At 291.5°C , the experimental mass loss (49 %) is very close to the theoretical value (47.8 %). Now the composition of the product will be $\text{Sb}[\text{CS}(\text{NH}_2)_2]\text{Br}$. If this composition is reasonable, the theoretical content of Sb in $\text{Sb}[\text{CS}(\text{NH}_2)_2]\text{Br}$ will be 43.8 %. A check experiment was conducted by heating the powder of single crystals of ATBM placed in an alumina crucible using a muffle furnace. After the furnace temperature rose to 292°C , the sample was kept in the furnace for 38 min. The mass loss (48.9 %) of the sample is very close to the theoretical mass loss (47.8 %). The atomic absorption spectroscopy using GBC 932 Plus of the heated sample indicates that the relative content of Sb (45.921 %) is close to the theoretical content of Sb in $\text{Sb}[\text{CS}(\text{NH}_2)_2]\text{Br}$. The elemental analysis of the heated sample was performed on a Flash EA1112 CHNS Analyzer (Thermo Electron Corp.). The elemental analysis results are summarized in Table 4, which

Table 4 Elemental composition in the decomposition product after heating at 292 °C using CHNS analyzer

Element	Theoretical composition (%)	Experimental composition (%)
C	4.32	4.11
H	1.45	1.37
N	10.08	9.34
S	11.54	10.99

**Fig. 4** FT-IR spectrum of decomposition product after heating ATBM at 292 °C

also demonstrate the validity of the chemical composition $\text{Sb}[\text{CS}(\text{NH}_2)_2]\text{Br}$. The FT-IR spectrum of this decomposition product is shown in Fig. 4. The absorptions at 1607.3 cm^{-1} , 1400.1 cm^{-1} , and 1088.3 cm^{-1} were due to NH_2 deformation modes, C–S stretching, and NH_2 rocking modes, respectively. The presence of water modes is due to the absorption of moisture by the product [21].

From $291.5\text{ }^\circ\text{C}$ to $366.9\text{ }^\circ\text{C}$, CSNH_2 (thiocarbazoyl group), HBr , and partial antimony atoms will be eliminated from the complex leading to the endothermic peak at $345.8\text{ }^\circ\text{C}$ on the DTA curve. At $366.9\text{ }^\circ\text{C}$, the experimental and theoretical mass losses are 82.1 % and 81.7 %, respectively. A check experiment was performed by heating the powder of single crystals of ATBM to $367\text{ }^\circ\text{C}$, and it was kept at that temperature for 17 min. The mass loss (82.9 %) of the sample is very close to the theoretical mass loss (81.7 %). The atomic absorption spectroscopy of the heated sample indicates that the relative content of Sb is 98.8 %. This shows that the product at $367\text{ }^\circ\text{C}$ is metal antimony which will be volatilized with temperature leading to zero mass. The FT-IR spectrum of this decomposition product is shown in Fig. 5. The thermal decomposition data are given in Table 5.

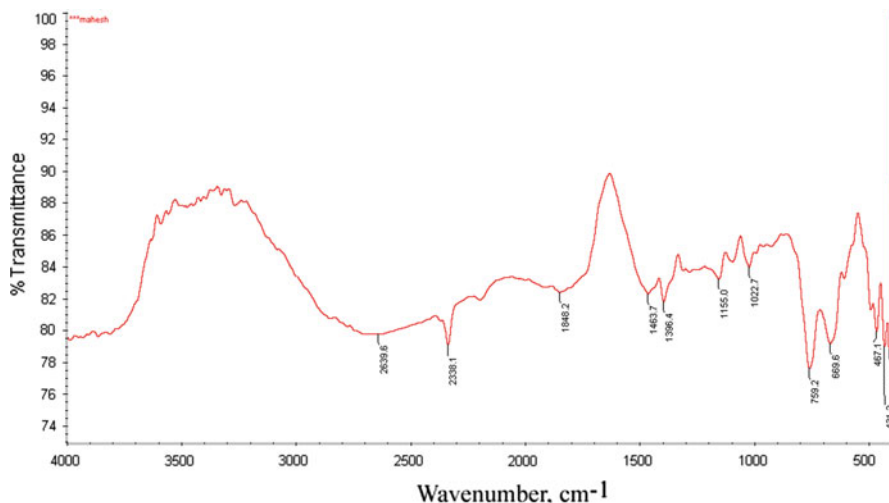


Fig. 5 FT-IR spectrum of decomposition product after heating ATBM at 367 °C

Table 5 Thermal decomposition data of ATBM crystal

Reaction	DTA (°C)	Mass loss (%)		Sb (%)	
		W_{exp}	W_{theor}	W_{exp}	W_{theor}
Sb[CS(NH ₂) ₂] ₂ Br ₃ ·H ₂ O					22.899
↓ -H ₂ O (94.4 °C–184.7 °C)	100.6 (endo)	4.038	3.388		
↓ Sb[CS(NH ₂) ₂] ₂ Br ₃					23.702
↓ -Br ₂ , -SC(NH ₂) ₂ (184.7 °C–291.5 °C)	264.7 (endo) 292	44.933 45.417 ^a	44.371		
↓ Sb[CS(NH ₂) ₂]Br				45.921 ^b	43.83
↓ -HBr, -CSNHNH ₂ , -0.2Sb (291.5 °C–366.9 °C)	345.8 (endo) 367	33.08 82.913 ^a	33.924		
↓ 0.8Sb				98.75 ^b	100
↓ -0.8Sb (366.9 °C–972.7 °C)		17.66	18.317		

^a Percentage mass loss of the sample measured in the check experiment

^b Relative content of Sb in the intermediate measured in the check experiment

4 Conclusions

The growth of ATBM single crystals is reported. The solution growth technique at room temperature is found suitable for growing ATBM single crystals. The FT-IR analysis reveals that the water of crystallization is weakly bonded in ATBM crystals.

The thermal analysis shows that there is no structure rearrangement or phase transformation in the complex before and after melting.

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