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Characterization and thermal analysis of thiourea and bismuth trichloride complex

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Abstract A complex of thiourea and bismuth trichloride has been synthesized. Its composition is $Bi_3Cl_9[SC(NH_2)_2]_7$. Crystallographic data are $a = 7.141(2)$ Å, $b = 8.820(3)$ Å, $c = 16.365(5)$ Å, $\alpha = 99.389(4)°$, $\beta = 95.422(4)°$, $\gamma = 106.177(4)°$, triclinic system. There are the mononuclear anion $[BiCl_5SC(NH_2)_2]^{2-}$ and the dinuclear cation $\{Bi_2Cl_4[SC(NH_2)_2]_6\}^{2+}$ with the Bi–Cl–Bi bridge bonds in the complex. The electric conductance of the absolute methanol solution contained the complex indicates that the complex is an ionic compound. Raman spectra indicate that the bismuth ion is coordinated by the sulfur atoms of the thiourea. The thermal analysis verifies the structure of complex. The TG–MASS curves show the structure rearrangement in the complex at about 118 °C. The DSC curves and calculation means that the structure rearrangement is irreversible.

Keywords Ionic compounds · Bismuth(III) chloride · Thiourea · Crystal structure · Raman spectroscopy · Thermal analysis · TG–DTA–MS · DSC

Introduction

The VA main group metal compounds including inorganic and metallorganic complexes have been studied for decades owing to the interesting physical properties, medical and material functions [1–8]. Bismuth nitrate and bismuth acetate of thiourea crystal complexes were reported with formula $Bi_2(CH_3COO)_6 \cdot 3SC(NH_2)_2 \cdot H_2O$, $Bi(CH_3COO)_3 \cdot 3SC(NH_2)_2$, $[Bi(NO_3)\{SC(NH_2)_2\}_5](NO_3)_2 \cdot H_2O$ and $[Bi(NO_3)_3\{SC(NH_2)_2\}_3]$ [9, 10]. Two kinds single crystal of bismuth thiourea chloride were synthesized with different formula. One of them was $[Bi(tu)_6][Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]_2$, which included the $[Bi(tu)_6]^{3+}$ cations and $[Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]_2^{3-}$ anions group [11]. Another of them was $Bi(tu)_3Cl_3$ [12]. Some bismuth complexes can be used in medicine, microbiology and pharmacology because of their special biological or medicinal functions [13–23]. With its features of highly variable coordination numbers and irregular coordination geometry, bismuth can form compounds with various structures and chemical bonding [24, 25]. Because inorganic salts of bismuth can be easily hydrolyzed in the aqueous solution [26], it is rather difficult to synthesize the solid complexes of the bismuth in the aqueous solution. We have found that some solid complexes of bismuth can be prepared easily through solid–solid reaction [27, 28]. Thermal analysis is important to study the chemical structure and the reaction course of the complex [29, 30]. This paper reports the complex of bismuth chloride and thiourea in the absolute methanol solution. The characterizations can demonstrate that the

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new complex is an ionic compound and possesses an interesting formula with the special cations and anions structure. We verify the structure of complex by thermal analysis. From the TG–MASS curves and DSC calculations, we find there is an irreversible structure rearrangement in the complex at about 118 °C.

Experimental

The bismuth trichloride and thiourea used were of analytical reagent and commercially purchased. Firstly, 3.0812 g (9.8 mmol) $BiCl_3$ were dissolved in 80 mL absolute methanol in a beaker. Then 2.236 g (29.4 mmol) thioureas were slowly added. The mixture was stirred for 2 h at room temperature. The solvent in the resultant solution was vaporized slowly in air for a week. Finally, the light yellow transparent crystal was obtained. The crystal is stable in the air (Table 1).

Carbon, hydrogen, nitrogen and sulfur in the complex were analyzed by an Elementar Vario El III elemental analyzer. XRD of the single crystal sample was carried out and the data were collected by SMART APEXCCD diffractometer. The refinement method was full-matrix least-squares on F^2. In all cases a semi-empirical absorption correction from equivalents was made. Hydrogen atoms were included at the calculated positions. The powder X-ray diffraction pattern of the sample which was obtained from annealing sample at 120 °C for 20 min was recorded by a D/max-2550 VB/PC X-ray powder diffractometer at room temperature. $CuK_{\alpha1}$ radiation was used for the XRD measurement. Data were collected with a scan step of $12°min^{-1}$ between 5° and 75°. The method for indexing is the least-square fitting. Electric conductance of the absolute methanol solution contained the complex was measured by DDS-307 Conductometer at 17 °C using DJS-1C electrode. Raman spectra of the complex, $BiCl_3$ and $SC(NH_2)_2$ were measured by a Renishaw in Via Reflex Laser Raman spectrometer (785 nm excitation). Thermal studies for the complex were performed by a NETZSCH STA 449C TG–DTA–MS Thermal Analyzer under argon atmospheric with a heating rate of 10 °C min^{-1}. The mass of the sample is 15.020 mg. TG–DTA, MS, DSC curves of the complex are shown in Figs. 4, 5 and 6, respectively. The experimental and calculated results for the thermal analysis are summarized in Table 3.

Table 1 Crystallographic data for complex

Empirical formula	$C_7H_{28}Bi_3Cl_9N_{14}S_7$
Formula weight	1478.84
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	7.141(2)
b (Å)	8.820(3)
c (Å)	16.365(5)
α (°)	99.389(4)
β (°)	95.422(4)
γ (°)	106.177(4)
Volume ($Å^3$)	965.9(6)
Z	1
Density, ρ (cal.) (Mg m^{-3})	2.542
λ (Mo K_α) (Å)	0.71073
Crystal size (mm^3)	0.15 × 0.10 × 0.10
Theta range for data collection (°)	1.28 to 25.5
Index ranges	$-8 \leq h \leq 8$ $-10 \leq k \leq 10$ $-19 \leq l \leq 11$
Reflections collected/unique	4278/3538 [R(int) = 0.0484]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0481$, $wR_2 = 0.1240$
R indices (all data)	$R_1 = 0.0527$, $wR_2 = 0.1262$

Results and discussion

The results of the element analysis for the product show that $C_{(exp.)}$ is 5.71%, $H_{(exp.)}$ is 1.90%, $N_{(exp.)}$ is 13.27% and $S_{(exp.)}$ is 15.22%. Therefore, the most possible formula of the resultant is $Bi_3Cl_9[SC(NH_2)_2]_7$. In this case, the relative content of C, H, N and S in $Bi_3Cl_9[SC(NH_2)_2]_7$ is $C_{(cal.)}$: 5.69%, $H_{(cal.)}$: 1.91%, $N_{(cal.)}$: 13.26% and $S_{(cal.)}$: 15.15%. The calculated results are very close to the measured ones.

As is shown in Figs. 1 and 2, the single-crystal X-ray diffraction of the complex indicates that the crystal structure of the complex belongs to triclinic system. There

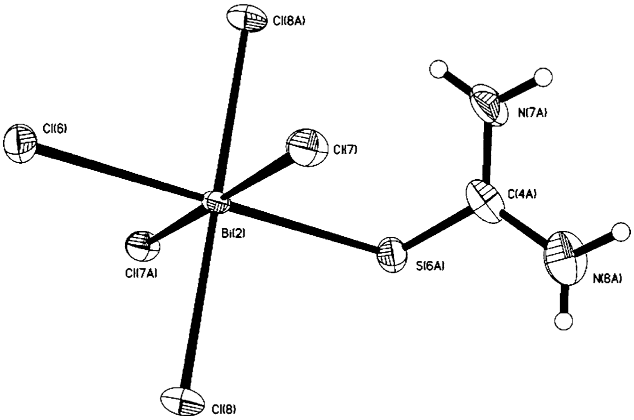


Fig. 1 The structure of the mononuclear $[BiCl_5SC(NH_2)_2]^{2-}$ group

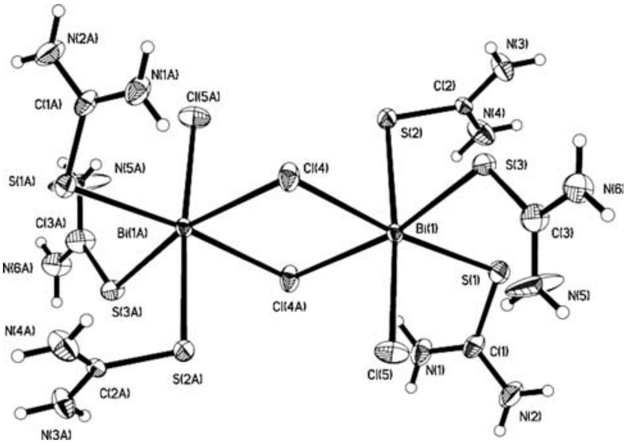


Fig. 2 The structure of the dinuclear $[Bi_2Cl_4(SC(NH_2)_2)_6]^{2+}$ group

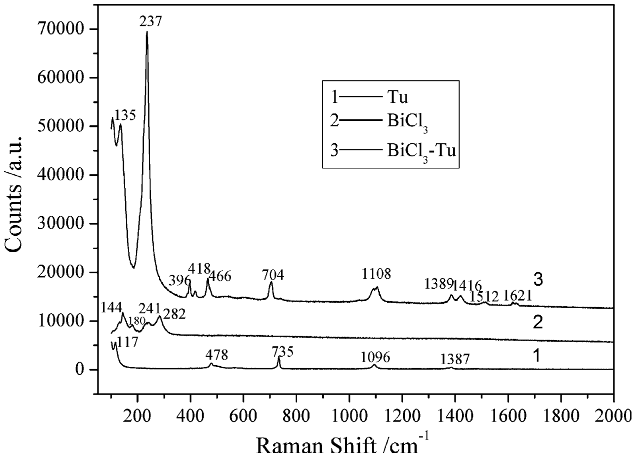


Fig. 3 Raman spectrum of $SC(NH_2)_2$, $BiCl_3$ and $Bi_3Cl_9[SC(NH_2)_2]_7$

are mononuclear $BiCl_5SC(NH_2)_2$ and dinuclear $Bi_2Cl_4(SC(NH_2)_2)_6$ group with two negative and positive charges. The metal ion is coordinated by the sulfur atom in most metal thiourea complexes and by the nitrogen atom in a few metal thiourea complexes [31, 32]. In the new complex, the bismuth ion is coordinated by the sulfur atom of thiourea.

The conductance measurement indicates that the conductivity of the absolute methanol solution contained the complex with the concentration 1.0×10^{-3} mol L^{-1} is 172.3 μS cm^{-1} at 17 °C. Obviously the conductivity of the complex solution is much higher than that (4.54 μS cm^{-1}) of the pure absolute methanol. The conductivity of the absolute methanol solution contained $BiCl_3$ with the concentration of 3.0×10^{-3} mol L^{-1} is 358 μS cm^{-1} at 17 °C. Each complex molecule contains three $BiCl_3$ and seven $SC(NH_2)_2$ molecules. Although the conductivity (358 μS cm^{-1}) of the $BiCl_3$ solution with the concentration 3.0×10^{-3} mol L^{-1} is much higher than that (172.3 μS cm^{-1}) of the complex solution, still much less than the three multiple values (516.9 μS cm^{-1}) of that (172.3 μS cm^{-1}) of the complex solution with the concentration of 1.0×10^{-3} mol L^{-1}. The conductivity of thiourea in the absolute methanol solution with the concentration of 7.0×10^{-3} mol L^{-1} is 4.9 μS cm^{-1}. This is very close to the conductivity (4.54 μS cm^{-1}) of the pure absolute methanol at 17 °C. So, we consider that the $[Bi_2Cl_4(SC(NH_2)_2)_6]^{2+}$ cation and $[BiCl_5SC(NH_2)_2]^{2-}$ anion in the complex might have made certain contribution to the conductance of the complex. The conductance results show that the complex is an ionic one.

Raman spectroscopy of thiourea, bismuth trichloride and complex are shown in Fig. 3. The symmetry of the thiourea molecule belongs to C_{2v} group. Many vibration modes in the molecule with C_{2v} symmetry are Raman active [33]. Generally, the stretching vibrations produce stronger Raman bands than the deformation vibrations, the chemical bonds containing heavier atoms produce stronger Raman bands than those containing lighter atoms, and the intensity of Raman scattering from the vibration of the double bond is much stronger than that from the single bond [33]. So, in Raman spectrum of thiourea Fig. 3(1), we assign the peak at 1387 cm^{-1} to the stretching vibration of the N–C–N bond, the peak at 478 cm^{-1} to the deformation vibration of the N–C–N bond and the peak at 1096 cm^{-1} to the rocking vibration of the NH_2 group. The intense peak at 735 cm^{-1} may be from the stretching vibration of the C=S double bond. The peak at 117 cm^{-1} may be from the lattice vibrations in the solid sample. As shown in Fig. 3(2), there are four peaks in Raman spectrum of bismuth trichloride: the symmetric or antisymmetric stretching vibration and the symmetric or antisymmetric deformation vibration. Usually, the symmetric vibration will produce stronger Raman band than antisymmetric vibration. In this case, we assign the peak at 282 cm^{-1} and peak at 241 cm^{-1} to the symmetric and asymmetric stretching vibration of the Bi–Cl bond, respectively, and the peak at 180 cm^{-1} to the symmetric deformation vibration of the Cl–Bi–Cl bond in bismuth trichloride. As for the peak at 144 cm^{-1}, perhaps, it can be attributed to the overlap of the peak from the antisymmetric deformation vibration of the Cl–Bi–Cl bond and the peak from the lattice vibration in the crystal, since it seems to be impossible that the strongest peak with a very low frequency is only from the antisymmetric deformation vibration of the Cl–Bi–Cl bond.

As is shown in Figs. 1 and 2, the mononuclear $[BiCl_5SC(NH_2)_2]^{2-}$ group and the dinuclear $[Bi_2Cl_4(SC(NH_2)_2)_6]^{2+}$ group are different both in coordination structure and symmetry. In the mononuclear $[BiCl_5SC(NH_2)_2]^{2-}$ group, five Cl atoms and one S atom coordinate with the Bi ion. The Bi ion is at the center of octahedra composed of the Cl and S atoms. From the corresponding bond lengths and bond angles in Table 2, we can find that the $BiCl_5S$ group is very similar to an octahedral MX_5Y-type molecule, to which, various vibration modes have been given [33]. In the dinuclear $[Bi_2Cl_4(SC(NH_2)_2)_6]^{2+}$ group, there are two Bi–Cl–Bi bridge bonds. Two Cl bridge atoms, one Cl anion and three S atoms from the thiouea molecules will bond to each Bi ion. According to the corresponding bond lengths and angles in Table 2, we can consider that the two Bi atoms and two Cl atoms in the two Bi–Cl–Bi bridge bonds are coplanar and the symmetry of the $S_3ClBi–(Cl)_2–BiClS_3$ group approximately belongs to C_2 group. Thus, we give the assignments for the peaks in Raman spectrum of the complex. In Fig. 3(3), some peaks from thiourea also appear in that of the complex, but will shifts. In Raman spectrum of the complex, there are some new peaks, such as peaks at 237, 396 and 466 cm^{-1}. It has been reported that the frequency of the stretching vibration of the M–S bond in the thiourea complexes of various metal ions is between 200 and 300 cm^{-1}. Therefore, the new peak with highest intensity at 237 cm^{-1} might be the stretching vibration of the Bi–S bond. The peaks at 396 and 418 cm^{-1} may be from various stretching vibrations of the Bi–Cl bonds with different bond lengths in the complex. As for the peak at 466 cm^{-1}, this may be from the "breathing" vibration of the four-member ring composed of two Bi–Cl–Bi bridge bonds. The symmetric "breathing" vibration can produce stronger Raman peak. The peak at 704 cm^{-1} can be assigned to the stretching vibration of the C=S bond. Due to the bonding between the S and Bi atoms, the effective mass of the S atom in the C=S bond may appear slightly larger. Therefore, the frequency (704 cm^{-1}) of the stretching vibration of the C=S bond in the complex molecule must be lower than that (733.5 cm^{-1}) of the C=S bond in the thiouea molecule. The peak at 1108 cm^{-1} and the peak at 1389 cm^{-1} in Raman spectrum of the complex may be from the rocking vibration of the NH_2 group and the stretching vibration of the N–C–N bond, respectively. However, due to the induction effect of the Bi–S bond, the peaks in the complex also shift. For example, the frequency (1096 cm^{-1}) of the rocking vibration of the NH_2 in thiouea is lower than that (1108 cm^{-1}) in the complex. In Fig. 3(3), the peaks at 1416, 1512 and 1621 cm^{-1} may be assigned to various stretching and deformation vibrations in the N–C–N bond and the NH_2 group, respectively. For the peak at 135 cm^{-1}, this may be from the lattice vibration in the complex crystal.

Table 3 lists the possible thermal decomposition reactions of the complex. As is shown in Fig. 4, there is a small endothermic peak at 118.08 °C in DTA curve of the complex. However, there is not any corresponding weight

Table 2 Selected bond lengths (Å) and angles (°) in the complex

Bi(1)–Cl(5)	2.6712(10)	Bi(2)–Cl(7A)	2.6987(10)
Bi(1)–S(3)	2.6761(9)	Bi(2)–Cl(7)	2.6987(10)
Bi(1)–S(1)	2.6871(9)	Bi(2)–Cl(8A)	2.7151(10)
Bi(1)–S(2)	2.7925(11)	Bi(2)–Cl(8)	2.7151(10)
Bi(1)–Cl(4)	2.9189(10)	Bi(2)–Cl(6A)	2.7564(10)
Bi(1)–Cl(4A)	2.9369(10)	Bi(2)–S(6A)	2.7564(10)
Cl(5)–Bi(1)–S(3)	99.76(2)	Cl(7A)–Bi(2)–Cl(7)	180.00(2)
Cl(5)–Bi(1)–S(1)	89.56(2)	Cl(7A)–Bi(2)–Cl(8A)	90.20(2)
S(3)–Bi(1)–S(1)	85.49(3)	Cl(7)–Bi(2)–Cl(8A)	89.80(2)
Cl(5)–Bi(1)–S(2)	175.19(2)	Cl(7A)–Bi(2)–Cl(8)	89.80(2)
S(3)–Bi(1)–S(2)	83.964(19)	Cl(7)–Bi(2)–Cl(8)	90.20(2)
S(1)–Bi(1)–S(2)	93.79(2)	Cl(8A)–Bi(2)–Cl(8)	180.00(2)
Cl(5)–Bi(1)–Cl(4)	90.89(2)	Cl(7A)–Bi(2)–Cl(6A)	87.89(2)
S(3)–Bi(1)–Cl(4)	84.88(3)	Cl(7)–Bi(2)–Cl(6A)	92.11(2)
S(1)–Bi(1)–Cl(4)	170.290(18)	Cl(8A)–Bi(2)–Cl(6A)	89.54(2)
S(2)–Bi(1)–Cl(4)	86.39(2)	Cl(8)–Bi(2)–Cl(6A)	90.46(2)
Cl(5)–Bi(1)–Cl(4A)	87.72(2)	Cl(7A)–Bi(2)–S(6A)	87.89(2)
S(3)–Bi(1)–Cl(4A)	168.118(17)	Cl(7)–Bi(2)–S(6A)	92.11(2)
S(1)–Bi(1)–Cl(4A)	103.92(3)	Cl(8A)–Bi(2)–S(6A)	89.54(2)
S(2)–Bi(1)–Cl(4A)	88.130(19)	Cl(7A)–Bi(2)–S(6)	92.11(3)
Cl(4)–Bi(1)–Cl(4A)	85.79(2)	Cl(8)–Bi(2)–S(6)	89.54(2)
Bi(1)–Cl(4)–Bi(1A)	94.21(2)	Cl(8A)–Bi(2)–S(6)	90.46(2)
Cl(7)–Bi(2)–S(6)	87.89(2)		

Table 3 Thermal decomposition data of $Bi_3Cl_9[SC(NH_2)_2]_7$

Reaction	T(DTA) (°C)	Mass loss (%)	
		$W_{exp.}$	$W_{theor.}$
$Bi_3Cl_9[SC(NH_2)_2]_7$			
↓ Structural rearrangement	118.08 (endo.)		
$Bi_3Cl_9[SC(NH_2)_2]_7$			
↓ Softening of crystal	170.37 (endo.)		
$Bi_3Cl_9[SC(NH_2)_2]_7$			
↓ $-2SC(NH_2)_2$			
↓ $-NH_2$, $-S$	214.89 (exo.)	13.85	13.55
$Bi_3Cl_9[SC(NH_2)_2]_4(CNH_2)$			
↓ $-SC(NH_2)_2$			
↓ $-NH_2$, $-S$			
↓ $-Cl$	299.17 (endo.)	10.60	10.79
$Bi_3Cl_8[SC(NH_2)_2]_2$			
↓ $-CNH_2$			
↓ $-S$, $-NH_2$			
↓ $-4Cl$, $-Cl_2$		20.85	20.62
$Bi_3Cl_2(CCNH_2)SC(NH_2)_2$			
↓ $-2HCl$		5.08	4.95
$Bi_3C(CNH_2)SC(NH_2)_2$			
↓ $-SC(NH_2)_2$			
↓ $-C(CNH_2)$			
↓ −0.53Bi	649.13 (endo.)	15.30	15.34
2.47Bi			
↓ −0.22Bi		3.13	3.11
2.25Bi		31.19[a]	31.80[b]

[a] The experimental percentage mass of the residue in the sample

[b] The calculated percentage mass of the residue in the sample

loss in TG curve of the complex and no ion current in mass curves at 118.08 °C in Fig. 5. Therefore, the small endothermic peak could be attributed to the structure rearrangement in the coordination sphere of the complex or the possible phase transformation in the crystal. To check whether the structure rearrangement or the phase transformation in the crystal occurs at about 118 °C, a certain amount (about 500 mg) of the solid complex was placed in an alumina crucible and heated at 120 °C for 20 min in a muffle furnace, and then, measure the powder X-ray diffraction pattern of the heat-treated sample. All the peaks in the X-ray diffraction pattern of the heat-treated sample can be very readily indexed by a set of lattice parameters and the relative deviations between the calculated and experimental d_{hkl} are <0.5%. It is obvious that the sample is a single-phase compound. The crystal structure of the heat-treated sample still belongs to the triclinic system with the lattice parameters: $a = 0.7158$ nm, $b = 0.8850$ nm, $c = 1.6431$ nm, $\alpha = 99.30°$, $\beta = 95.41°$ and $\gamma = 106.14°$. The lattice parameters of the heat-treated sample are very close to that of the single crystal of the complex. This shows that the change on the cell of the complex crystal is very small. Besides, the DSC measurement indicates that the reaction heat for the change of complex at 118.08 °C is 6.542 kJ mol^{-1}. This is much less than the phase transformation heat of the solid compound. General speaking, the reaction heat for the phase transformation in most solid compounds is tens to several hundred kJ mol^{-1}. In this case, we can consider that the endothermic peak at 118.08 °C in DTA curve of the complex can be attributed to the structure rearrangement in the complex, not to the phase transformation in the crystal. We measured the DSC

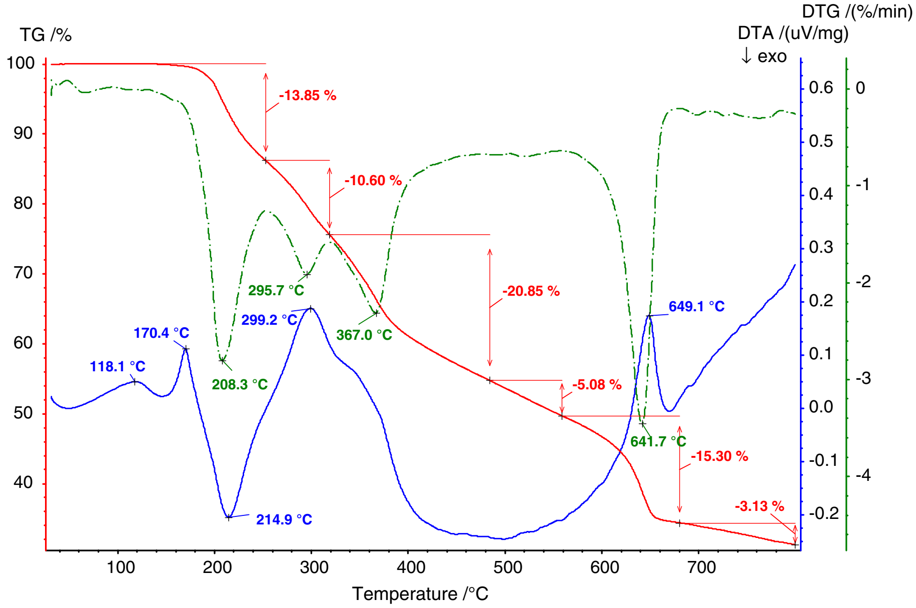
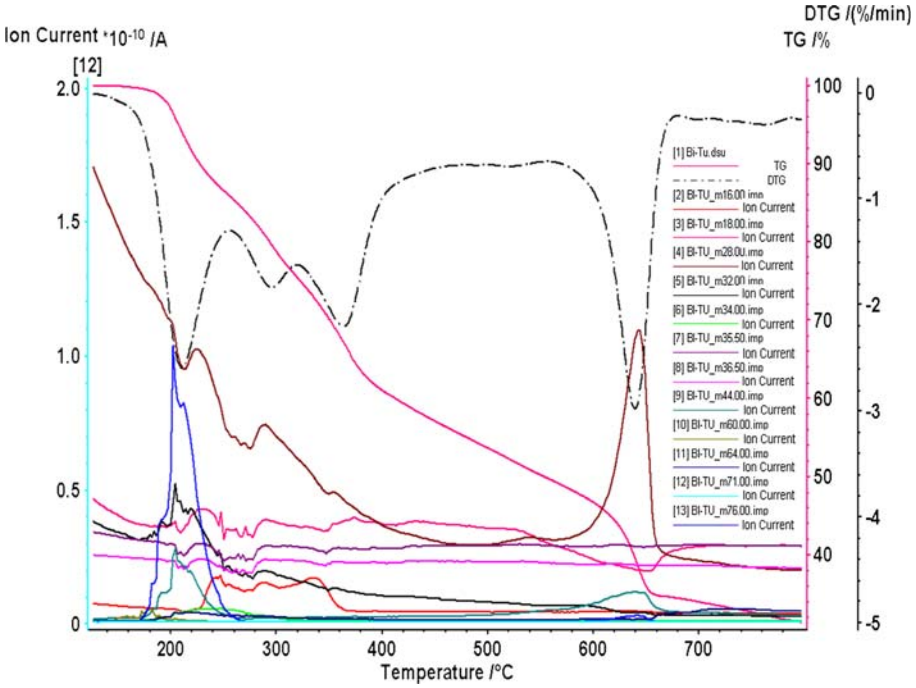


Fig. 4 TG–DTG–DTA curves of the complex $Bi_3Cl_9[SC(NH_2)_2]_7$

Fig. 5 MS curve of the complex $Bi_3Cl_9[SC(NH_2)_2]_7$



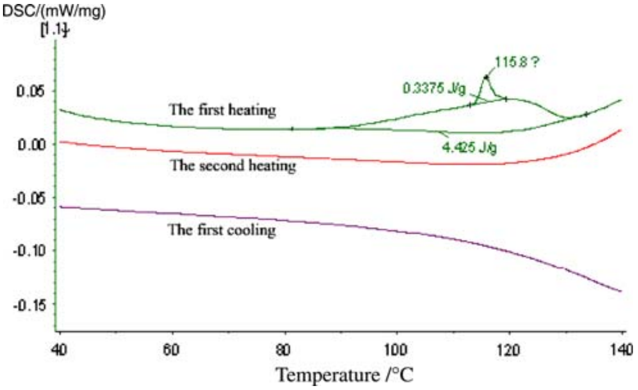


Fig. 6 DSC curves of the complex $Bi_3Cl_9[SC(NH_2)_2]_7$

of complex by the first heating, the first cooling and the second heating progress. In Fig. 6, we noted that there is an endothermic peak at 115.8 °C in the first heating, but no corresponding exothermic peak in the first cooling. Compared with the first heating, there is no endothermic peak in the second one. This means that structure rearrangement in the complex crystal is irreversible. Then, an apparent endothermic peak in DTA curve appears at 170.37 °C, again, before the thermal decomposition of the complex begins. Since there is not any corresponding weight loss of the sample in the TG curve at about 170 °C, this may be due to softening of the solid sample. In fact, to heat the crystal sample in capillary can demonstrate that the softening point of the solid complex is at about 170 °C. The first weight loss of the sample happens at about 200 °C corresponding to an exothermic peak at about 214 °C in DTA curve. In MS curves of the pyrolysis products, there are the peaks of the species: $SC(NH_2)_2$ ($m/z = 76$), CS ($m/z = 44$), S ($m/z = 32$) and NH_2 ($m/z = 16$). If two $SC(NH_2)_2$ molecules, one S atom and one terminal NH_2 group of the thiourea molecule are eliminated from the sample at this step, the theoretical weight loss (13.55%) is close to the experimental one (13.85%). Usually, the thermal decomposition process of the complex in the inert gas always leads to the endothermic peak in DTA curve, as the breaking of chemical bond needs certain energy. However, why is there an exothermic peak at about 214 °C in DTA curve of the new complex? Perhaps, the eliminations of the $SC(NH_2)_2$, S atom and terminal NH_2 group from the solid complex will lead to the structure rearrangement and to the formation of new chemical bonds in the residual sample. If the total bond energy of the formed chemical bonds is larger than that of the broken chemical bonds, this can also lead to an exothermic peak in DTA curve of the sample. Soon afterwards, the sample will lose one $SC(NH_2)_2$ molecule, one S atom and one terminal NH_2 group, again. Meanwhile, one Cl atom is also eliminated from the complex molecule. The above conclusion can also be supported by MS curves of the pyrolysis products. In this case, the calculated theoretical weight loss (10.80%) matches very well with the experimental one (10.60%). Then, there is a larger weight loss (20.85%) in the range from 320 to 480 °C in TG curve of the sample. In this stage, a lot of Cl atoms will be eliminated from the complex. In addition, one $SC(NH_2)_2$ molecule and two terminal

NH_2 group will also be eliminated. We have noted that the pyrolysis products contain both four free Cl atoms and one Cl_2 molecule. Why are there two kinds of chlorines in the pyrolysis products? As is mentioned above, there are a lot of hydrogen bonds (N–H···Cl) in the lattice of the complex. Therefore, some Cl atoms exist in the solid complex in the form of the Cl···HNH···Cl groups, and some in the form of the Bi–Cl–Bi bridge bonds. Perhaps, different Cl atoms in the lattice of the complex will produce the different pyrolysis products. And above 500 °C, the sample loses the two residual Cl atoms. Finally, the sample loses the last thiourea ligand and becomes the metal Bi. When temperature is over 600 °C, the metal Bi will gradually volatilize. The volatilization of the metal needs certain energy; hence, there is an apparent endothermic peak at 649.13 °C in DTA curve. The thermal decomposition product is the black residue with metallic luster.

Conclusions

The complex of bismuth and thiourea is synthesized through a liquid reaction in the absolute methanol solution of thiourea and bismuth trichloride. The complex is composed of a mononuclear $[BiCl_5SC(NH_2)_2]^{2-}$ anion and a dinuclear $[Bi_2Cl_4(SC(NH_2)_2)_6]^{2+}$ cation group. The conductance of the absolute methanol solution contained the complex shows that the complex is an ionic compound. The thermal analysis verifies the structure of complex. From the TG–MASS curves, there is a structure rearrangement in the complex at about 118 °C. The DSC curves and calculation shows that the structure rearrangement is irreversible.

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