

THERMAL DECOMPOSITION OF TRIS(*N,N*-DISUBSTITUTED DITHIOCARBAMATE) COMPLEXES OF As(III), Sb(III) AND Bi(III)

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Thermal studies on tris(*N,N*-disubstituted dithiocarbamates) of arsenic(III), antimony(III) and bismuth(III) of the type $M[S_2CX]_3$ ($M = As, Sb, Bi; X = NEt_2, N(CH_2)_4O$) by simultaneous TG, DTG and DTA were carried out in air and nitrogen atmospheres. The apparent activation energies were determined by the graphical method of Freeman-Carroll, modified for $n = 1$, and Piloyan's two methods from the TG and DTG curves. The TTN temperatures were calculated from the TG profiles.

A possible mechanism of the decomposition reaction is suggested on the basis of the results of their pyrolysis and their mass spectral data.

The intermediates obtained at the ends of various decomposition stages were identified via elemental analysis and i. r. and mass spectral data, whereas the residues were identified by X-ray powder diffraction analysis. A dimeric structure of the type $M_2[S_2CN(CH_2)_4O]_4$ ($M = As, Sb$) is proposed.

A literature survey reveals that little work has been done on thermal studies of metal dithiocarbamate complexes, especially of the group V_A elements [1, 2].

As a continuation of our previous work on metal dithiocarbamates [3], we describe here the thermal investigation of tris(*N,N*-disubstituted dithiocarbamates) as As(III), Sb(III) and Bi(III) under the general formula $M[S_2CX]_3$ ($X = NEt_2, N(CH_2)_4O$).

Simultaneous TG/DTG/DTA studies in dynamic atmospheres of air and nitrogen are reported and discussed. The results of pyrolysis, E^* values for the first stage of decomposition, derived from the Freeman-Carroll [4] and Piloyan methods [5], TTN calculations [6], and a proposed mechanism of the decomposition reaction are also reported and discussed.

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Experimental

All complexes were prepared by known methods [7, 8]; they were recrystallized from a mixture of CH_2Cl_2 – $\text{C}_2\text{H}_5\text{OH}$, and dried under vacuum. The thermal decomposition was carried out on a Netsch 429 derivatograph at a heating rate of 2 deg/min, in the temperature range 20–600°, with a sample mass of 25 mg and α - Al_2O_3 as reference. The measurements were performed in dynamic atmospheres of air and nitrogen.

X-ray powder diffraction analyses of the final residues were made with a Phillips PW 1130/00 X-ray diffractometer, using $\text{CuK}\alpha$ radiation. For the determination of TTN, the areas of the TG curves were measured with a Coradi Cora–Senior planimeter.

Carbon, hydrogen and nitrogen determinations were performed on a Perkin–Elmer 240 microanalyser. Infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin–Elmer 467 spectrophotometer, using KBr pellets. Mass spectra were recorded on an R. M. V.-6L–Hitachi–Perkin–Elmer mass spectrometer. Molecular weight measurements were made on a Perkin–Elmer 115 molecular weight apparatus.

Pyrolysis

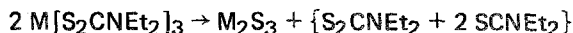
The pyrolysis of all complexes was carried out in dynamic nitrogen atmosphere using the same technique as applied in our earlier work [3]. Highly volatile products of decomposition, such as CS_2 , were collected in a liquid air trap. The less volatile components of decomposition were separated by column chromatography, and were identified by spectroscopic methods (i. r., M. S.), elemental analyses and molecular weight determinations.

Results and discussion

Thermal analysis

All thermal curves (TG, DTG and DTA) of tris(diethyldithiocarbamate) complexes are given in Figs 1–6. It can be seen that in all cases the decomposition process in air, over the temperature range from 20 to 600°, includes various thermal effects. The temperature ranges and percentage mass losses of the decompositions are given in Tables 1 and 2. The temperatures of the greatest rate of decomposition (DTG_{max}), the theoretical percentage mass losses, and the DTA data are also given.

The first decomposition stage is attained after the melting point and involves a sudden and considerable loss of mass (58–74%). This is attributed to the evolved moieties $\{\text{S}_2\text{CNEt}_2 + 2\text{SCNEt}_2\}$, according to the following reaction:



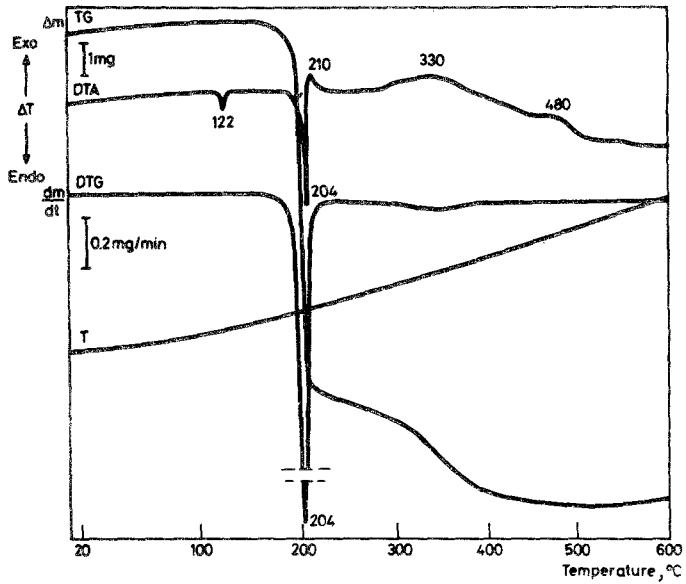


Fig. 1 Thermal curves for $\text{As}[\text{S}_2\text{CNEt}_2]_3$ in air

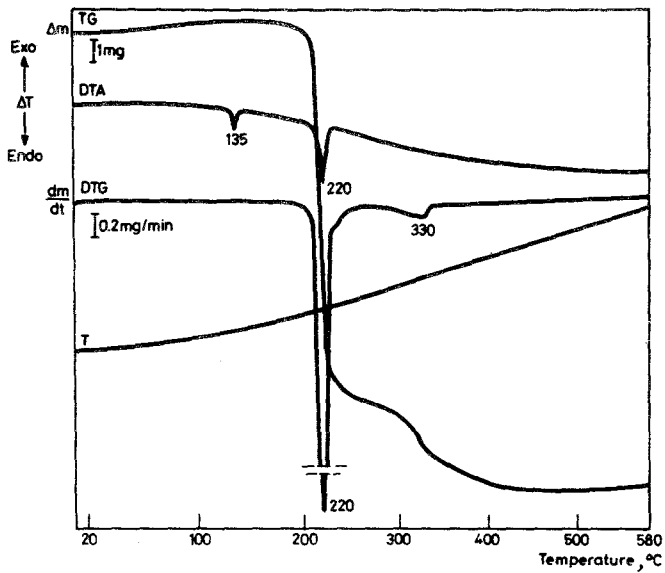


Fig. 2 Thermal curves for $\text{As}[\text{S}_2\text{CNEt}_2]_3$ in nitrogen

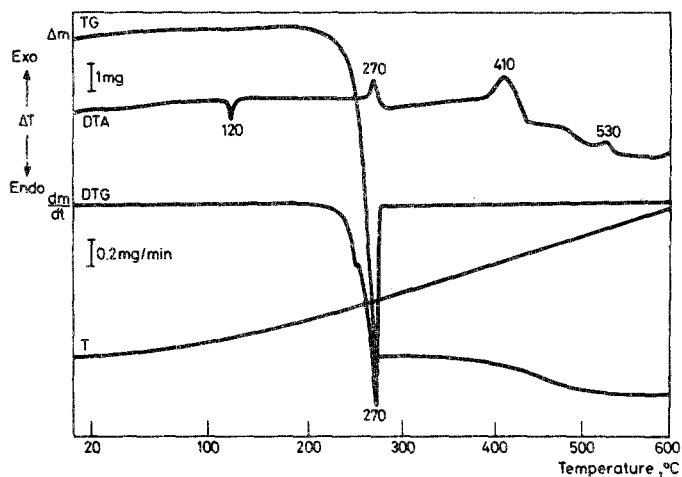


Fig. 3 Thermal curves for $\text{Sb}[\text{S}_2\text{CNEt}_2]_3$ in air

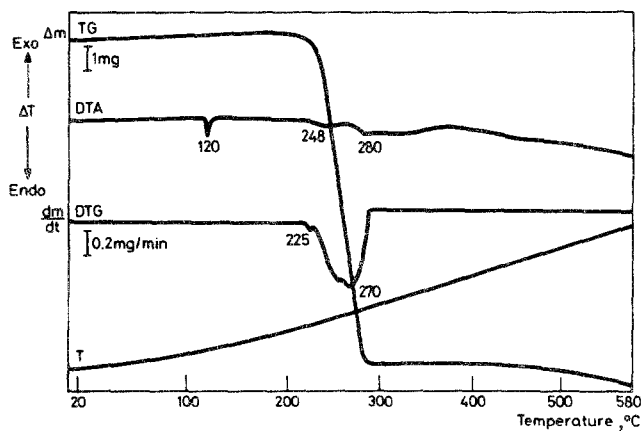


Fig. 4 Thermal curves for $\text{Sb}[\text{S}_2\text{CNEt}_2]_3$ in nitrogen

Metal sulfides, M_2S_3 ($\text{M} = \text{As}, \text{Sb}, \text{Bi}$), are the possible intermediates after the first decomposition stage in both air and nitrogen, and have been found as final residues in nitrogen.

In the case of the arsenic complex, the As_2S_3 is oxidized to As_4O_6 in the second stage; its sublimation occurs in the third stage, leaving the crucible without a residue. Both the second and the third stages are exothermic, at 330° and 480° , respectively. In the case of the antimony and bismuth complexes, the Sb_2S_3 is oxidized to Sb_2O_4 and the Bi_2S_3 to $(\text{BiO})_2\text{SO}_4$, both of which are stable up to 600° and give a plateau

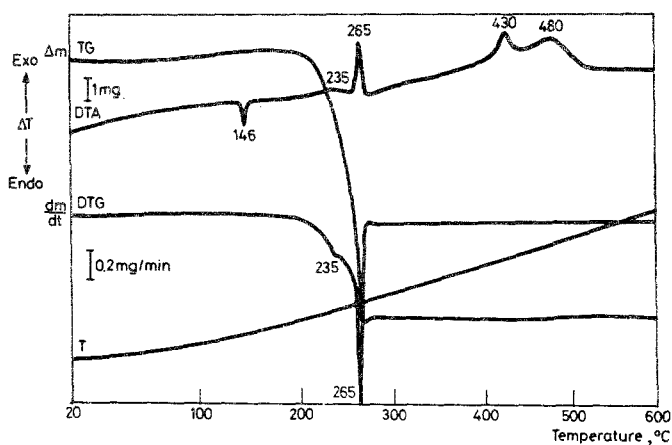


Fig. 5 Thermal curves for $\text{Bi}[\text{S}_2\text{CNEt}_2]_3$ in air

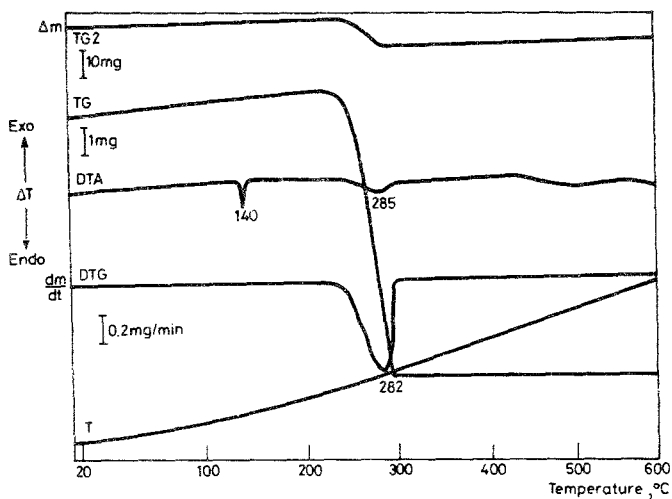


Fig. 6 Thermal curves for $\text{Bi}[\text{S}_2\text{CNEt}_2]_3$ in nitrogen

in the TG curve. All the final products were identified by X-ray powder diffraction analysis.

The thermal curves (TG, DTG and DTA) of the tris(morpholinodithiocarbamate) complexes of As, Sb and Bi are depicted in Figs 7–12. The thermal analysis data obtained from these curves are given in Tables 3 and 4. From the TG profiles, it is obvious that the first and main decomposition stage is common in both air and nitrogen, and begins without melting of the complexes. The considerable mass losses in this stage (59–74%) involve the elimination of one dithiocarbamate group plus two

Table 1 Thermal analysis results (TG/DTG/DTA) on tris(diethylthiocarbamates) of As(III), Sb(III) and Bi(III) in air atmosphere

| Complex | DTA results | | | TG/DTG results | | | | | Mass calcd., % |
|--|----------------------------------|---|--------------|--------------------------|----------------|-----------------|--|-------|----------------|
| | m. p., °C endothermic peak | peak temperature, °C endothermic (-) exothermic (+) | stage | temperature range, °C | DTG max. °C | mass loss, % | Evolved moiety formula | | |
| As[S ₂ CNEt ₂] ₃ | 122 | 204 (-), 210 (+) | 1 | 165-220 | 204 | 73.8 | S ₂ CNEt ₂ + 2 SCNEt ₂ | 73.21 | |
| | | 330 (+) | 2 | 280-380 | 330 | 10.0 | As ₂ S ₃ → As ₂ O ₃ | 9.25 | |
| | | 480 (+) | 3 residue | 380-500 > 500 | | 17.3 0 | As ₂ O ₃ (As ₄ O ₆) | 19.08 | |
| Sb[S ₂ CNEt ₂] ₃ | 120 | 270 (+) | 1 | 200-270 | 245, 270 | 69.2 | S ₂ CNEt ₂ + 2 SCNEt ₂ | 67.10 | |
| | | 410 (+) | 2 | 320-520 | | 5.2 | Sb ₂ S ₃ → Sb ₂ O ₄ | 5.65 | |
| | | 530 (+) | residue | > 520 | | 25.6 | Sb ₂ O ₄ | 27.20 | |
| Bi[S ₂ CNEt ₂] ₃ | 146 | 235 (+), 265 (+) | 1 | 200-270 | 235, 265 | 57.8 | S ₂ CNEt ₂ + 2 SCNEt ₂ | 58.18 | |
| | | 430 (+) | | | | | | | |
| | | 480 (+) | residue | > 480 | | 41.8 | (BiO) ₂ SO ₄ | 41.80 | |

Table 2 Thermal analysis results (TG/DTG/DTA) on trisdiethylthiocarbamates of As(III), Sb(III) and Bi(III) in nitrogen atmosphere

| Complex | DTA results | | | TG/DTG results | | | | | Mass calcd., % |
|--|-------------|----------------------------------|----------------------------------|----------------|-----------------------|-------------------------|--------------|---|----------------|
| | m. p., °C | endothermic peak temperature, °C | peak endothermic temperature, °C | stage | temperature range, °C | DTG _{max} , °C | mass loss, % | Evolved moiety formula | |
| As[S ₂ CNEt ₂] ₃ | 135 | | 220 | 1 | 180-240 | 220 | 72.6 | S ₂ CNEt ₂ + 2 SCNEt ₂ | 73.21 |
| | | | | 2 | 280-340 | 330 | 9.2 | As ₂ S ₃ decomposition or | 23.69 |
| | | | | 3 | 340-440 | | 9.6 | As ₂ S ₂ volatility | 20.61 |
| Sb[S ₂ CNEt ₂] ₃ | | | | residue | > 440 | | ~ 0 | | — |
| | 120 | | 248, 280 | 1 | 200-285 | 270 | 69.2 | S ₂ CNEt ₂ + 2 SCNEt ₂ | 67.10 |
| | | | | 2 | 400-600 | | 3.6 | — | — |
| Bi[S ₂ CNEt ₂] ₃ | | | | residue | > 600 | | 27.2 | Sb ₂ S ₃ + Sb | 27.20 |
| | 140 | | 285 | 1 | 230-300 | 282 | 58.0 | S ₂ CNEt ₂ + 2 SCNEt ₂ | 58.18 |
| | | | | residue | > 420 | | 40.8 | Bi ₂ S ₃ | 39.35 |

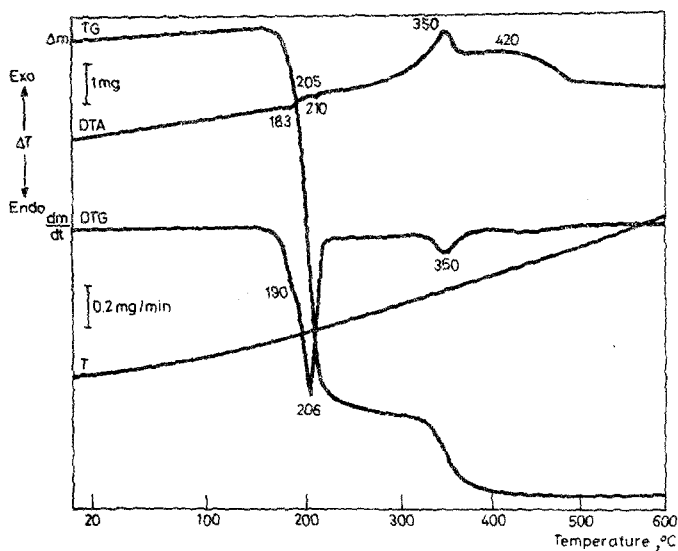


Fig. 7 Thermal curves for $\text{As}[\text{S}_2\text{CN}(\text{CH}_2)_4\text{O}]_3$ in air

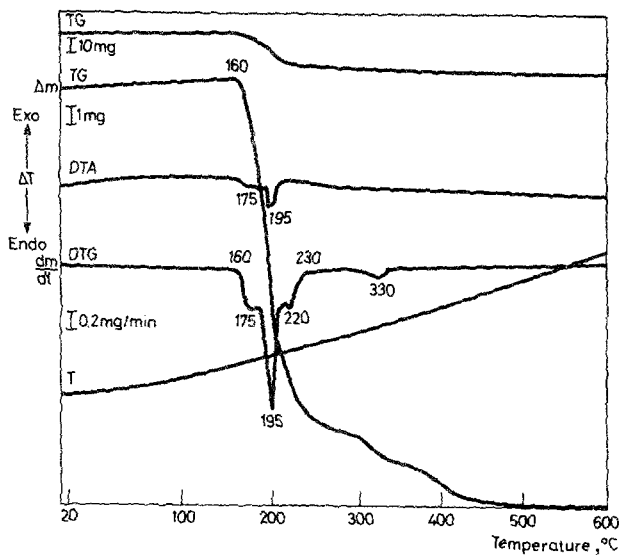


Fig. 8 Thermal curves for $\text{As}[\text{S}_2\text{CN}(\text{CH}_2)_4\text{O}]_3$ in nitrogen

thiocarbamoylo groups, as in the case of the diethyldithiocarbamate complexes described above.

However, the DTG curves of the dithiocarbamate complexes of morpholine show that the main decomposition process consists of two or three consecutive steps. It is

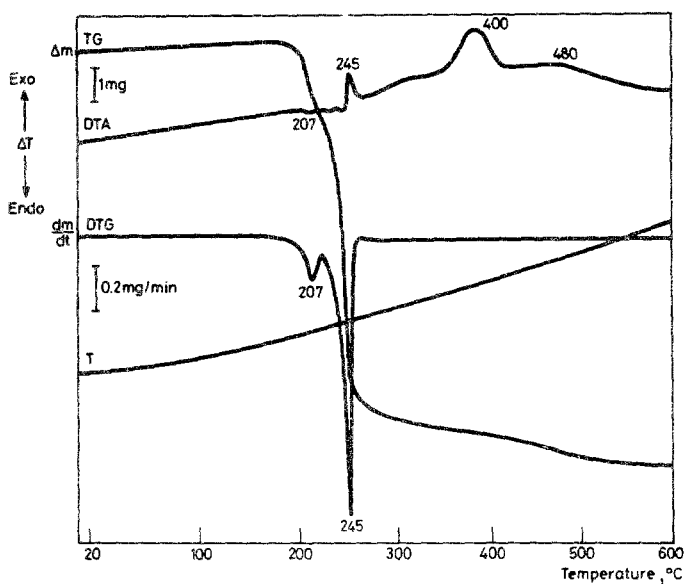


Fig. 9 Thermal curves for $\text{Sb}[\text{S}_2\text{CN}(\text{CH}_2)_4\text{O}]_3$ in air

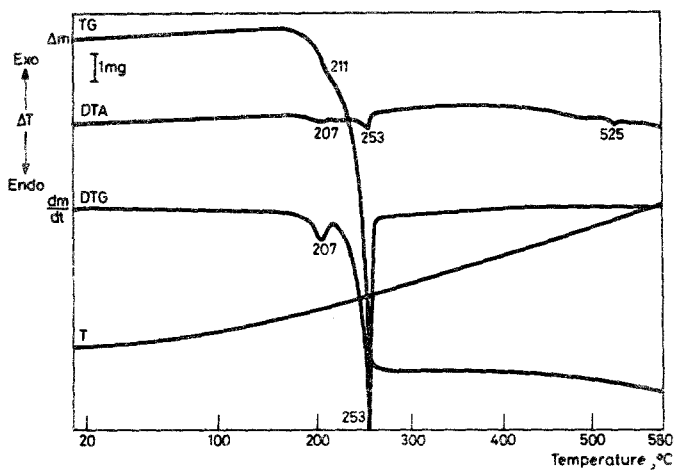


Fig. 10 Thermal curves for $\text{Sb}[\text{S}_2\text{CN}(\text{CH}_2)_4\text{O}]_3$ in nitrogen

logical to assume that carbon disulfide is primarily evolved after breaking of the metal-sulfur bond, which occurs first (Table 4, stage 1α), followed by elimination of the morpholino group of one ligand, plus one or two (Table 4, stage 1β) thio-carbamoylo moieties of the remaining ligands. The possible intermediates after the

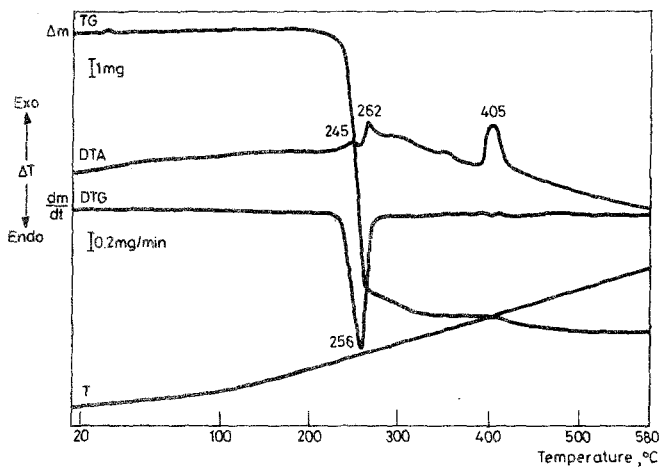


Fig. 11 Thermal curves for $\text{Bi}[\text{S}_2\text{CN}(\text{CH}_2)_4\text{O}]_3$ in air

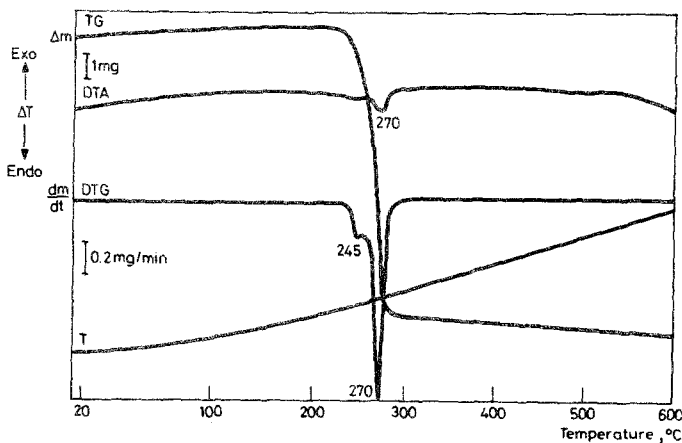


Fig. 12 Thermal curves for $\text{Bi}[\text{S}_2\text{CN}(\text{CH}_2)_4\text{O}]_3$ in nitrogen

first stage in both air and nitrogen are considered to be M_2S_3 , which were found as residual metal sulfides in nitrogen, in accord with our previous results [3].

In air, at higher temperatures, the second stage of decomposition involves the oxidation of metal sulfides, as in the case of the diethyldithiocarbamate complexes. In the case of the arsenic complex, there is also a third stage, in which the possibly formed As_4O_6 is gradually sublimed up to the end of the experiment at 600° .

The whole procedure of the thermal decompositions of the studied complexes with the same ligand depends on the nature of the metal. This was established by deter-

Table 3 Thermal analysis results (TG/DTG/DTA) on tris(morpholinodithiocarbamates) of As(III), Sb(III) and Bi(III) in air atmosphere

| Complex | DTA results | | | TG/DTG results | | | | Evolved moiety formula | Mass calcd., % |
|---|-------------|------------------------------|---------|-----------------------|-------------|--------------|-------------|--|----------------|
| | m. p., °C | peak temperature, °C | stage | temperature range, °C | DTG max. °C | mass loss, % | DTG max. °C | | |
| As[S ₂ CN(CH ₂) ₄ O] ₃ | — | 183 (-), 210 (-), 205 (+) | 1 | 160-220 + | 206 | 73.8 | 206 | S ₂ CN(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 74.86 |
| | | 350 (+) | 2 | 220-310 | 350 | 5.9 | | S | 5.70 |
| | | broad ~ 420 (+) | 3 | 310-390 | | 9.4 | | As ₂ S ₃ → As ₂ O ₃ | 8.55 |
| | | | residue | 390-500 | | 10.8 | | As ₂ O ₃ (As ₄ O ₆) | 17.64 |
| | | | residue | > 500 | | 0 | | | |
| As[S ₂ CN(CH ₂) ₄ O] ₃ | — | | 1 | 170-260 | 245 | 68.0 | 245 | S ₂ CN(CH ₂) ₄ O + SCN(CH ₂) ₄ O | 69.40 |
| | | 207 (-) 245 (+) | α. | 170-215 | 207 | 13.0 | 207 | CS ₂ | 12.50 |
| | | 400 (+) | β. | 215-260 | 245 | 55.0 | 245 | N(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 56.90 |
| | | | residue | 320-520 > 520 | | 7.2 | | Sb ₂ S ₃ → Sb ₂ O ₄ Sb ₂ O ₄ | 5.26 25.32 |
| Bi[S ₂ CN(CH ₂) ₄ O] ₃ | — | 245 (+), 262 (+) | 1 | 220-270 | 256 | 54.4 | 256 | S ₂ CN(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O + N(CH ₂) ₄ O | 54.37 |
| | | 405 (+) | 2 | 270-340 | | 5.8 | | CS | 6.33 |
| | | | residue | 380-460 > 460 | ~ 405 | 2.7 | | Bi ₂ S ₃ → (BiO) ₂ SO ₄ (BiO) ₂ SO ₄ | 39.28 37.0 |

Table 4. Thermal analysis results (TG/DTG/DTA) on tris(morpholinodithiocarbamates) of As(III), Sb(III) and Bi(III) in nitrogen atmosphere

| Complex | DTA results | | | TG/DTG results | | | | Evolved moiety formula | Mass calcd., % |
|---|----------------------------|----------------------------------|-----------|-----------------------|------------|--------------|---|------------------------|----------------|
| | m. p., °C endothermic peak | peak temperature, °C endothermic | stage | temperature range, °C | DTGmax, °C | mass loss, % | | | |
| As[S ₂ CN(CH ₂) ₄ O] ₃ | — | — | 1 | 160–230 | 195 | 73.8 | S ₂ CN(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 74.86 | |
| | | 175 | α. | 160–180 | 175 | 14.0 | CS ₂ | 13.54 | |
| | | 195 | β. | 180–200 | 195 | 39.0 | N(CH ₂) ₄ O + SCN(CH ₂) ₄ O | 38.49 | |
| | | — | γ. | 200–230 | 220 | 21.0 | SCN(CH ₂) ₄ O | 23.17 | |
| | | — | 2 residue | 230–500 > 500 | ~ 350 | 24.0 | As ₂ S ₃ | 21.92 | |
| Sb[S ₂ CN(CH ₂) ₄ O] ₃ | — | — | 1 | 170–260 | 253 | 68.0 | S ₂ CN(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 69.40 | |
| | | 207 | α. | 170–215 | 207 | 11.8 | CS ₂ | 12.50 | |
| | | 253 | β. | 215–260 | 253 | 56.2 | N(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 56.90 | |
| | | 525 | 2 residue | 440–540 > 540 | | 2.8 | 1/2 S | 2.63 | |
| | | — | | | | 27.8 | Sb ₂ S ₃ | 27.94 | |
| Bi[S ₂ CN(CH ₂) ₄ O] ₃ | — | — | 1 | 220–290 | 270 | 60.2 | S ₂ CN(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 60.70 | |
| | | 245 | α. | 220–250 | 245 | 8.2 | CS ₂ | 10.93 | |
| | | 270 | β. | 250–290 | 270 | 52.0 | N(CH ₂) ₄ O + 2 SCN(CH ₂) ₄ O | 49.77 | |
| | | — | 2 residue | 290–520 > 520 | | 2.3 | 1/2 S | 2.30 | |
| | | — | | | | 37.0 | Bi ₂ S ₃ | 36.97 | |

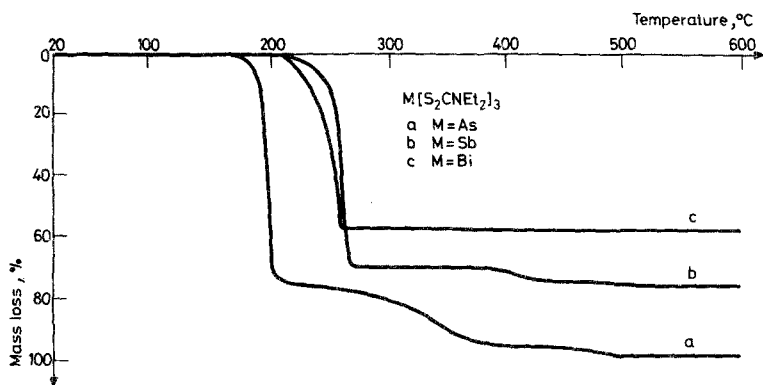


Fig. 13 Corrected TG curves for tris(diethyldithiocarbamates) in air

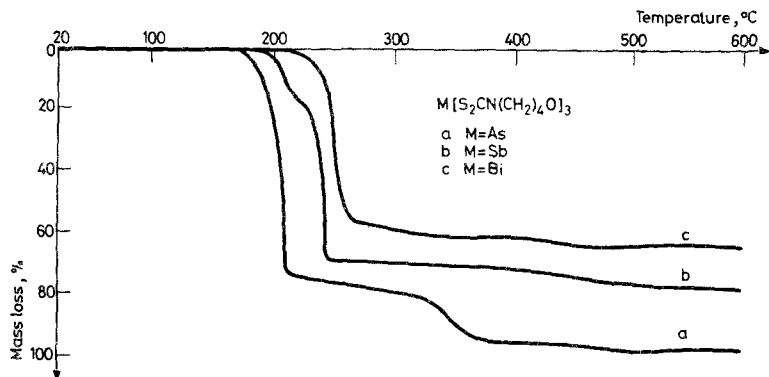


Fig. 14 Corrected TG curves for tris(morpholinodithiocarbamates) in air

Table 5 Activation energies, E^* , of some dithiocarbamate complexes

| Complex | Activation energy, E^* , kJ/mol | | |
|---|-----------------------------------|---------------|----------------|
| | Freemman-Carroll ($n = 1$) | Piloyan TG | Piloyan DTG |
| Sb[S ₂ CNEt ₂] ₃ | 231 | 168 | 239 |
| Bi[S ₂ CNEt ₂] ₃ | 181 | 151 | 134 |
| As[S ₂ CN(CH ₂) ₄ O] ₃ | 239 | 231 | 189 |
| Sb[S ₂ CN(CH ₂) ₄ O] ₃ | — | 105 | — |
| Bi[S ₂ CN(CH ₂) ₄ O] ₃ | 273 | 181 | — |

$M[S_2CNEt_2]^{-1\ddagger}$, whereas, especially for the Bi(III) complex, there are fragments corresponding to polynuclear compounds of the type M_nS_m , as in the case of the piperidyldithiocarbamate complexes.

Pyrolysis

Pyrolysis of $M[S_2CNEt_2]_3$ ($M = As, Sb, Bi$)

The sample was heated in nitrogen atmosphere up to the temperature of the end of the first and main decomposition stage. The volatile products formed during the pyrolysis of the tris(diethyldithiocarbamate) complexes were CS_2 and a yellow liquid which turned out to be tetraethylthiocarbamyl sulfenamide [11].

The diethylammonium salt of diethyldithiocarbamic acid, $Et_2NCS_2^-H_2N^+\ddagger Et_2$, was also isolated as a white solid, which is unstable in air and decomposes to diethylamine [12, 13]. The nature of the volatile pyrolysis products of the tris(diethyldithiocarbamate) complexes of As, Sb and Bi reveals that their thermal decomposition is similar to that of the corresponding tris(piperidyldithiocarbamates). However, neither the derivative of thiourea with diethylamine nor the dimeric compounds $[Et_2NCS_2]_2M-M[S_2CNEt_2]_2$ were isolated. It is highly possible that the compounds are formed, but we have been unable to isolate them due to their instability at these temperatures.

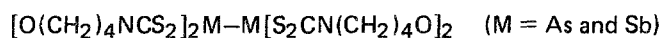
After the completion of pyrolysis at 250° , all complexes leave a black residue at the bottom of the flask, in which the respective sulfides of the trivalent metals (M_2S_3) were detected. Elemental carbon (1–9%) was also detected in the residues.

Pyrolysis of the black residue from the complex $Sb[S_2CNEt_2]_3$ was continued at higher temperature (330°), and afforded small amounts of a volatile product, which was identified as ethyl *N,N*-diethyldithiocarbamate, $Et_2N-C(:S)-S-Et$.

Pyrolysis of $M[S_2CN(CH_2)_4O]_3$ ($M = As, Sb, Bi$)

These complexes decompose suddenly, without melting, and give as the most volatile product CS_2 , which was detected in the liquid air trap. A white solid, in large amounts, was identified as the dimorpholinium salt of morpholinodithiocarbamic acid, $O(CH_2)_4NCS_2^-H_2N^+(\ddagger)(CH_2)_4O$, analogously as in the cases of the diethyl and piperidinodithiocarbamates of the same metals. As the decomposition proceeds further, the derivative of thiourea with morpholine, $O(CH_2)_4N-C(:S)-N(CH_2)_4O$, was also detected, but not the corresponding sulfenamide.

On the addition of ethanol to the chloroform solution of the mixture of volatile pyrolysis products of the studied complexes, a light-brown solid was precipitated. This was formulated as the following dimeric species:



Similar behaviour was noticed in our previous study of piperidinodithiocarbamates [3]. Analysis of the corresponding compound of arsenic(III) fits well the expected results

which decomposes further to the volatile products *a*, *b* and *c*. However, there is the possibility of elimination primarily of CS₂ and N(CH₂)₄O, which gives the salt (*a*). This means the simultaneous breaking of the M–S and C–N bonds. Also, the absence of the morpholinodithiocarbamate ester, RS–C(:S)N(CH₂)₄O (R = alkyl), from the pyrolysis product, suggests that the morpholinodithiocarbamate ligands behave as bidentate ones even at higher temperatures.

Formation of the dimeric compounds M₂[S₂CN(CH₂)₄O]₄ (M = As and Sb) is an important event in the thermal decomposition of the studied complexes. From these dimers, on further heating, the metal sulfides are produced. As expected, the Bi(III) analogue was not isolated.

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Zusammenfassung – *N,N*-Disubstituierte Tris-dithiocarbamate von Arsen(III), Antimon(III) und Wismut(III) des Typs M[S₂CX]₃ (M = As, Sb, Bi; X = NEt₂, N(CH₂)₄O) wurden simultan mittels TG, DTG und DTA in Luft- und Stickstoffatmosphäre untersucht. Die scheinbaren Aktivierungsenergien wurden nach der für *n* = 1 modifizierten graphischen Methode von Freemann–Carroll und nach den zwei Methoden von Piloyan aus den TG- und DTG-Kurven ermittelt. Die TTN-Temperaturen wurden aus den TG-Profilen berechnet. Ein möglicher Zersetzungsmechanismus wird basierend auf Ergebnissen der Pyrolyse und massenspektrometrischen Daten vorgeschlagen. Die nach den verschiedenen Zersetzungsstufen vorliegenden Zwischenprodukte wurden mittels Elementaranalyse sowie infrarot- und massenspektrometrischen Daten, der Rückstand durch Röntgenpulverdiffraktometrie identifiziert. Es wird eine dimere Struktur des Typs M₂[S₂CN(CH₂)₄O]₄ (M = As, Sb) vorgeschlagen.

Резюме — Трис(*N,N*-дизамещенные дитиокарбаматы) трехвалентных мышьяка, сурьмы и висмута типа $M\{S_2CX\}_3$, где $M = As, Sb, Bi$; а $X = NEt_2, N(CH_2)_4O$, были изучены совмещенными методами ТГ, ДТГ и ДТА в атмосфере воздуха и азота. Кажущиеся энергии активации были определены графическим методом Фримена–Кэрролла, модифицированного для $n = 1$, а также двумя методами Пилояна на основе кривых ТГ и ДТГ. ТНН температуры были вычислены из профилей кривых ТГ. На основе полученных результатов пиролиза и масс-спектроскопических данных, предложен возможный механизм разложения исследованных комплексов. Промежуточные продукты, получаемые в конце различных стадий разложения, были идентифицированы элементарным анализом, ИК и масс-спектроскопией, тогда как конечные продукты реакции — порошковым рентгено-дифракционным анализом. Предложена димерная структура типа $M_2[S_2CN(CH_2)_4O]_4$, где $M = As, Sb$.