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THERMAL DECOMPOSITION OF Bi(III), Cd(II), Pb(II) AND Cu(II) THIOCYANATES

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Abstract

Thermal decomposition of $Bi(SCN)_3$, $Cd(SCN)_2$, $Pb(SCN)_2$ and $Cu(SCN)_2$ has been studied. The thermal analysis curves and the diffraction patterns of the solid intermediate and final products of the pyrolysis are presented. The gaseous products of the decomposition (SO_2 and CO_2) were detected and quantitatively determined. Thermal, X-ray and chemical analyses have been used to establish the nature of the reactions occurring at each stage in the decomposition.

Keywords: decomposition of $Bi(SCN)_3$, $Cd(SCN)_2$, $Pb(SCN)_2$ and $Cu(SCN)_2$, DTA, DTG, pyrolysis, TG, X-ray

Introduction

Simple metal thiocyanates are intermediate products of thermal decomposition of analytically significant thiocyanatobismuthates(III) [1] and thiocyanatochromates(III) [2, 3]. They subsequently decompose and stoichiometric amounts of sulfur dioxide are released. The sulfur dioxide can be determined by titration, spectrophotometry, potentiometry or conductometry. On these grounds methods of determination of milligram and microgram amounts of thiocyanates by thermal decomposition of copper(I) thiocyanates [4] and silver thiocyanates [5] were developed. Thermal methods of determination of thiocyanates are noteworthy due to their high selectivity and possibility of simultaneous determination of thiocyanate and chlorate anions.

Reactions of thermal decomposition of thiocyanates may also be used to determine cations which form sparingly soluble thiocyanates. One of the examples is thermo-alkalimetric method of determination of copper and silver, which involves precipitation of CuSCN and AgSCN and thermal decomposition of these compounds [6]. A thermal method was also developed to determine caesium by precipitation of $Cs[Bi(SCN)_4]$, thermal decomposition of the compound and alkalimetric determination of sulfur dioxide released as a results of the decomposition [7].

Investigation of reactions of thermal decomposition of simple thiocyanates may also help to explain the mechanism of thermal decomposition of complex thiocyan-

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atobismuthates and thiocyanatochromates with different metals in the outer coordination sphere.

Experimental

Preparation

$Bi(SCN)_3$, $Cd(SCN)_2$, $Pb(SCN)_2$ and $Cu(SCN)_2$ were prepared according to the methods described in the literature [8–11].

Apparatus

Thermal analysis curves of the compounds under study were made using an OD-102/1500°C derivatograph. The 100 mg samples were heated over the temperature range of 20–1000°C at a rate of 5°C min^{-1}. TG sensitivity 100 mg. α-Al_2O_3 was used as reference material. X-ray analysis of the compounds and their sinters was carried out by means of a Siemens D5000 diffractometer, using CuK_α radiation monochromatized by means of a secondary graphite monochromator. The curves were recorded over 2θ angle range 2–90° with scan step 0.04° and time of scan step 1 s.

Chromatograms of gases released as a result of decomposition of the thiocyanates under study were made by heating the sample at a rate of 10°C min^{-1} within the temperature range of 20–600°C using air as the carrier gas.

Sulfur dioxide was absorbed in washers filled with sodium tetrachloromercurate solution and determined by alkalimetry [12]. Carbon dioxide was adsorbed on ascarite and determined by gravimetry.

Thermal analysis

The thermal analysis curves of the examined compounds are shown in Fig. 1. The small mass loss observed on TG curves at lower temperatures result from the drying of the hygroscopic samples.

TG and DTG curves for $Bi(SCN)_3$ (Fig. 1a) indicate a three-stage decomposition of the compound. Each consecutive stage corresponds with a higher exothermic peak with maxima at 170, 270 and 430°C. The sample mass remains practically unchanged within the temperature range of 500–850°C and decreases slowly over 850°C.

$Cd(SCN)_2$ decomposes in four stages (Fig. 1b). The first three stages correspond with exothermic peaks at 160°C (low, broad), 300°C (high, sharp) and 580°C (sharp). The fourth stage corresponds with a small but sharp endothermic peak.

Figure 1c presents thermal analysis curves for $Pb(SCN)_2$. The analysis of TG and DTG curves indicates that the decomposition of this compound proceeds also in four stages corresponding with DTA peaks at 220 (exothermic), 320 (exothermic), 480 (exothermic) and 970°C (endothermic), higher than the respective peaks of cadmium thiocyanate. At the same time, the mass loss in each of the stages of decomposition is lower than that determined on the basis of TG curve of $Cd(SCN)_2$.

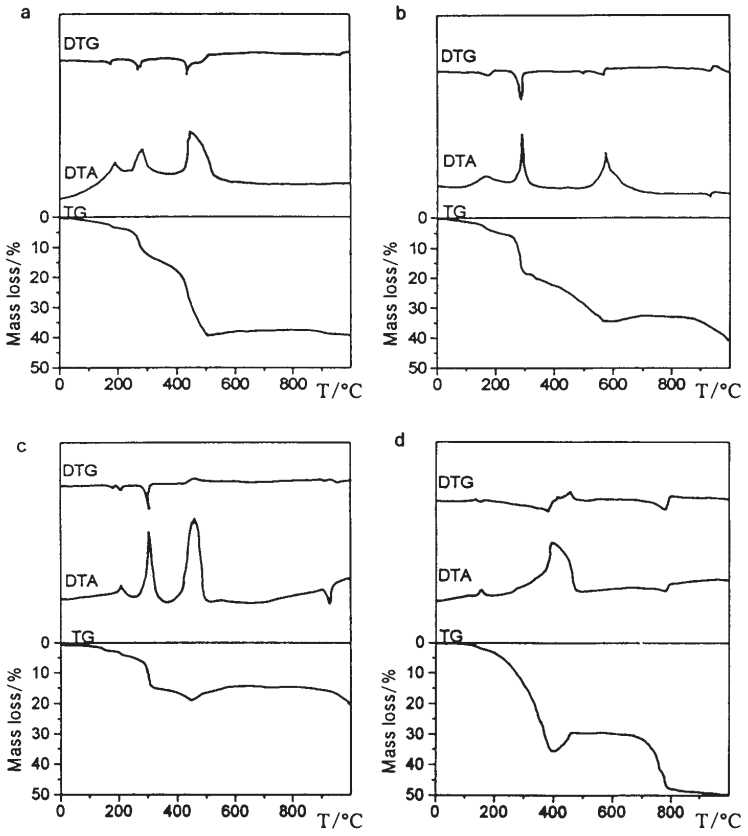

Fig. 1 Thermal decomposition curves of: a – $Bi(SCN)_3$; b – $Cd(SCN)_2$; c – $Pb(SCN)_2$; d – $Cu(SCN)_2$

The course of the thermal decomposition of copper(II) thiocyanate (Fig. 1d) is different from that of the above discussed compounds. The first stage of the reaction, which starts at 120°C corresponds with a slight mass loss on TG curve and a small exothermic peak on DTA curve at 160°C. At the second stage, a high mass loss and a broad DTA peak with a maximum at 400°C can be observed. An increase of mass occurs within the temperature range of 400–480°C. The last stage of the reaction preceeds over the temperature range of 650–800°C. It corresponds with a 28% mass loss and endothermic DTA peak at 780°C.

Analysis of intermediate and final products of thermal decomposition

In order to examine the course of thermal decomposition of the compounds under study, 100 mg samples were heated in an electric furnace in air atmosphere at

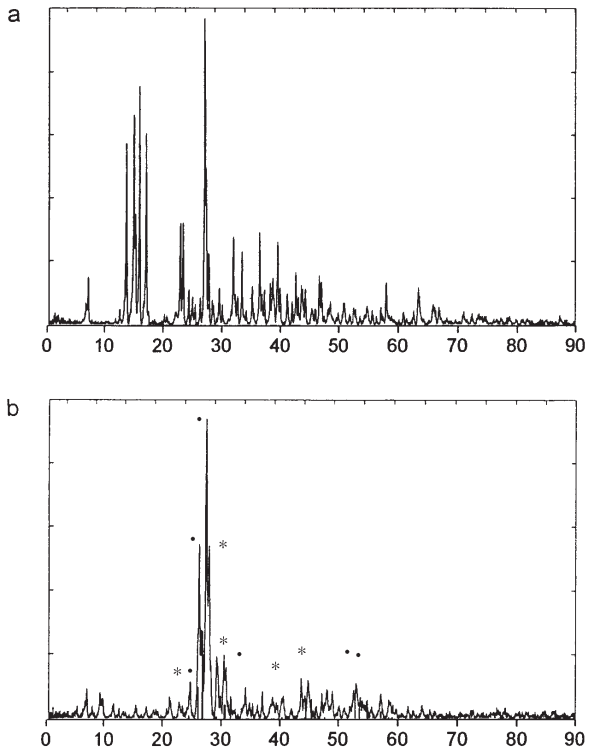

Fig. 2 Diffractions patterns of a – $Bi(SCN)_3$; b – its sinter at 600°C. • – Bi_2O_3; ∗ – $(BiO)_2SO_4$

5°C min^{-1} up to of characteristic temperatures determined from the TG curves. Diffractograms of the compounds and their sinters are presented in Figs 2–5.

Sulfur dioxide and carbon dioxide liberated during the thermal decomposition of thiocyanates were determined by the methods described above. The results are presented in Tables 1 and 2.

Table 1 Average results of determination of SO_2 released while thermal decomposition of thiocyanates

Compound	SO_2 determined/%	SO_2 calculated/%
$Bi(SCN)_3$	43.2	44.6
$Cd(SCN)_2$	27.8	28.0
$Pb(SCN)_2$	21.2	19.8
$Cu(SCN)_2$	24.8	23.8

Table 2 Average results of determination of CO_2 released while thermal decomposition of thiocyanates

Compound	CO_2 determined/%	CO_2 calculated/%
$Bi(SCN)_3$	35.7	34.5
$Cd(SCN)_2$	38.7	35.5
$Pb(SCN)_2$	27.3	27.2
$Cu(SCN)_2$	25.2	24.5

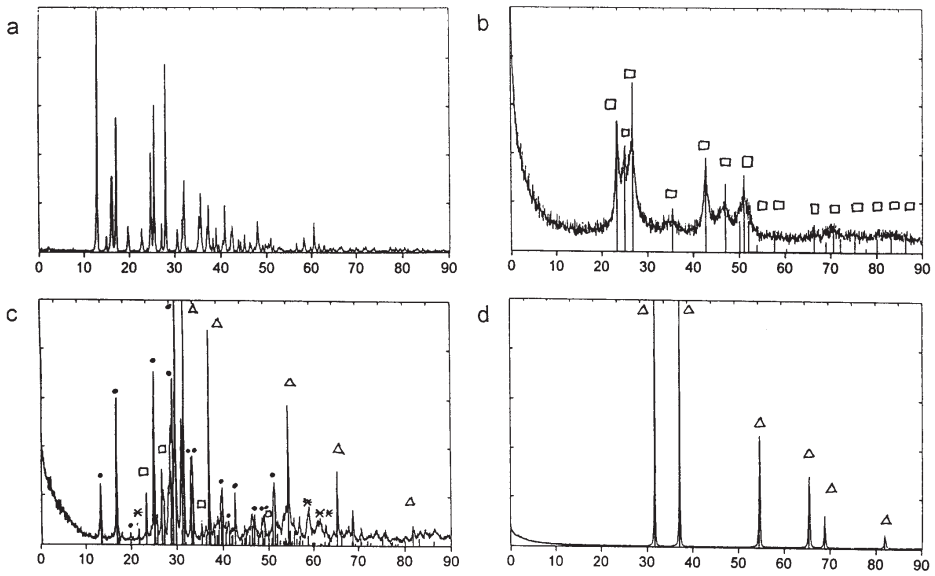

Fig. 3 Diffractions patterns of a – $Cd(SCN)_2$; b – its sinter at 380°C; c – its sinter at 700°C; d – its sinter at 1000°C. □ – CdS; Δ – CdO; ∗ – $CdSO_4$; • – $Cd_3O_2SO_4$

Discussion

The results of the thermal and X-ray analyses as well as the analysis of the gaseous products indicate that the first stage of thermal decomposition of $Bi(SCN)_3$ occurs in the temperature range of 120–180°C, according to the following scheme of reaction [13]:

$$6Bi(SCN)_3+3O_2 \rightarrow Bi(CN)_3\cdot 5Bi(SCN)_3+3SO_2 \quad (1)$$

The mass loss determined from the TG curve and calculated according to Eq. (1) are 4.5 and 4.2%, respectively.

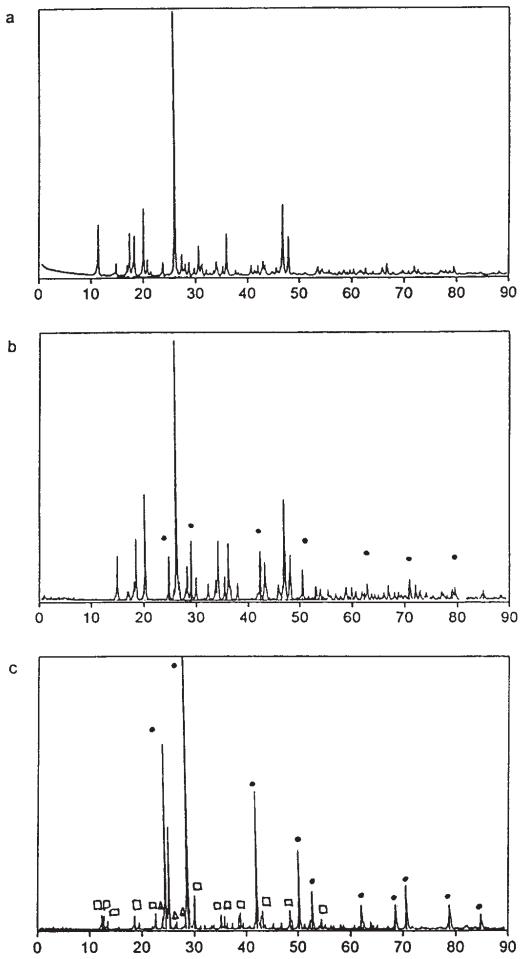

Fig. 4 Diffractions patterns of a – $Pb(SCN)_2$; b – its sinter at 240°C; c – its sinter at 600°C. • – PbS; □ – $Pb_2O(SO_4)$; Δ – $PbSO_4$

The products of the second stage of decomposition (240–300°C) are bismuth sulfide and a compound of bismuth, sulfur, carbon and nitrogen, with uncertain stoichiometric composition:

$$Bi(CN)_3 \cdot 5Bi(SCN)_3 + nO_2 \rightarrow Bi_2S_3 + 4BiS_xC_yN_z + \text{gaseous products} \quad (2)$$

Diffractograms of the sinter obtained by heating $Bi(SCN)_3$ up to 600°C indicate the presence of Bi_2O_3 and $(BiO)_2SO_4$, while SO_2 and CO_2 were found and determined in the liberated gases. The results of analyses indicate that bismuth thiocyanate, heated to 600°C decomposes according to the following reaction:

$$6Bi(SCN)_3 + 41.5\ O_2 \rightarrow 2(BiO)_2SO_4 + Bi_2O_3 + 16SO_2 + 18CO_2 + 9N_2 \quad (3)$$

The amount of SO_2 calculated on the basis of Eq. (3) is 44.6, while that determined experimentally 43.2%. The amounts of CO_2 are 34.4 and 35.7%, respectively.

At temperatures of over 900°C, bismuthyl sulfate decomposes [13], according to the following reaction:

$$(BiO)_2SO_4 \rightarrow Bi_2O_3+SO_3 \quad (4)$$

Thermal decomposition of $Cd(SCN)_2$ starts at about 130°C. Chromatographic analysis demonstrated that at 300°C all gaseous products are released, and X-ray analysis showed that the only solid decomposition product is cadmium sulfide (Fig. 3b). The amounts of SO_2 (27.8%) and CO_2 (38.7%) determined in the gaseous products are in accordance with the amounts calculated according to Eq. (5) (SO_2 – 28.0%, CO_2 – 38.5%).

$$Cd(SCN)_2+3O_2 \rightarrow CdS+SO_2+2CO_2+N_2 \quad (5)$$

Further heating of $Cd(SCN)_2$, connected with a slight increase of the sample mass, leads to oxidation of CdS (exothermic DTA peak at 580°C) according to the following equation:

$$CdS+2O_2 \rightarrow CdSO_4 \quad (6)$$

The X-ray pattern of the sinter obtained at 700°C indicates the presence of the following compounds: $CdSO_4$, CdS, $Cd_3O_2(SO_4)$ and CdO (Fig. 3c). At higher temperatures (>830°C) sulfates and oxysulfates decompose, SO_3 is liberated and the final solid product of thermal decomposition of cadmium thiocyanate is CdO (Fig. 3d).

Thermal decomposition of $Pb(SCN)_2$ is very similar to that of $Cd(SCN)_2$. It starts at 140°C. In the sinter obtained at 240°C, X-ray analysis demonstrated only the presence of PbS (Fig. 4b). The analysis of gaseous products liberated rapidly at about 320°C (peak at 320°C on the chromatogram) indicates the following course of the first stage of thermal decomposition reaction of $Pb(SCN)_2$:

$$Pb(SCN)_2+3O_2 \rightarrow PbS+SO_2+2CO_2+N_2 \quad (7)$$

The amounts of SO_2 and CO_2 determined (21.2 and 27.3% of the initial sample mass) are close to those calculated from Eq. (7) (19.8 and 27.2% respectively).

The increase of the sample mass over the temperature range 460–600°C results from oxidation of lead(II) sulfide to lead sulfate (exothermic DTA peak at 480°C).

$$PbS+2O_2 \rightarrow PbSO_4 \quad (8)$$

Diffractometric analysis of the sinter prepared by heating $Pb(SCN)_2$ to 600°C indicates that, apart from $PbSO_4$, it also contains $Pb_2(SO_4)O$ and slight amounts of PbS (Fig. 4c). Over 900°C the TG curve exhibits further decrease of the sample mass. The final solid product of thermal decomposition is lead(II) oxide.

Thermal decomposition of lead(II) thiocyanate over the temperature range of 20–1000°C may be presented as the following summary equation:

$$Pb(SCN)_2+5O_2 \rightarrow PbO+SO_2+SO_3+2CO_2+N_2 \quad (9)$$

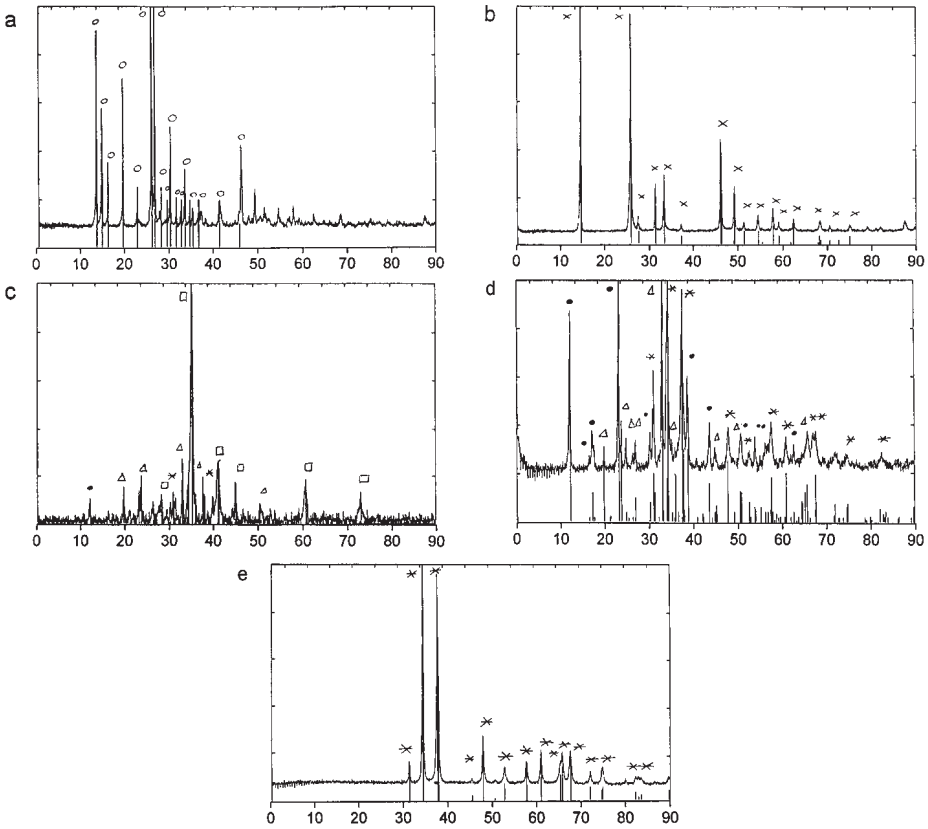

Fig. 5 Diffractions patterns of a – $Cu(SCN)_2$; b – its sinter at 170°C; c – its sinter at 400°C; d – its sinter at 530°C; e – its sinter at 850°C. o – $Cu(SCN)_2$; × – CuSCN; •– Cu_2OSO_4; Δ – $CuSO_4$; □ – Cu_2O; * – CuO

The first stage of decomposition of $Cu(SCN)_2$, which starts at about 120, corresponds with a DTA peak at 170°C. Diffraction patterns (Fig. 5b) of the sinter demonstrated the presence of CuSCN which is confirmed by Wendtland's [14] and Söderback's [15] theory's that at lower temperatures Cu(II) is reduced to Cu(I). A highly hygroscopic $Cu(SCN)_2$ reacts with H_2O according to the following reaction:

$$6Cu(SCN)_2+4H_2O \rightarrow 6CuSCN+5HSCN+HCN+H_2SO_4 \quad (10)$$

While heating above 200°C a broad exothermic peak on DTA appears as a result of two consecutive decomposition reactions. The first, connected with the mass loss ~35%, is an effect of decomposition of CuSCN according to the reaction:

$$6CuSCN+11O_2 \rightarrow 2Cu_2S+2CuO+4SO_2+6CO_2+3N_2 \quad (11)$$

The second one, represented by approriate peaks on DTA, TG and DTG curves, results in oxidation of Cu_2S.

On the diffraction pattern of sinter obtained at 400°C (Fig. 5c) apart peaks characteristic of the products of both above-mentioned decomposition reactions peaks characteristic of Cu_2O are present. Over the temperature range of 380–450°C, a 7% increase of sample mass is observed on the TG curve, related to oxidation of CuS to $CuSO_4$. On the diffraction patterns of the sinter obtained at 530°C (Fig. 5d) peaks characteristic of CuO, $CuSO_4$ and Cu_2OSO_4 are present. Over the temperature range of 650–800°C, the sample mass decreases, first slowly and then at a gradually growing rate, which is connected with the decomposition of copper sulfate and oxysulfate to CuO. Diffractometric analysis of the sinter obtained at 850°C (Fig. 5e) indicates, that the only final product of thermal decomposition of $Cu(SCN)_2$ is copper(II) oxide CuO.

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