ELSEVIER

Thermochimica Acta 359 (2000) 23–28

thermochimica acta

www.elsevier.com/locate/tca

Thermal decomposition of analytically important thiocyanatochromates(III)

Part 3

Elżbieta Skiba[*], Bogdan Ptaszyński

Institute of General and Ecological Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland

Received 20 September 1999; received in revised form 17 February 2000; accepted 19 February 2000

Abstract

The thermal decomposition of crystalline complex salts $Cu_3[Cr(SCN)_6]$ and $Cd_3[Cr(SCN)_6]_2 \cdot 8H_2O$ has been studied. On the basis of the thermal analysis of these compounds and the X-ray diffraction and chemical analyses of the products of their thermal decomposition, reaction products have been established. Thermal stability of the compounds has been compared.

Keywords: Thermal decomposition; Thiocyanatochromates(III); DTA; TG; DTG; X-ray analysis

1. Introduction

The present work is the continuation of a series of studies on thermal decomposition of hexathiocyanatochromates(III). In our previous reports [1,2], we discussed thermal decomposition of the following compounds: $Ag_3[Cr(SCN)_6]$, $Tl_3[Cr(SCN)_6]$, $Hg_3[Cr(SCN)_6]_2$, $Pb_3[Cr(SCN)_6]_2$ and $Bi[Cr(SCN)_6]$.

The subject of the present report is the synthesis and investigation of the reactions of thermal decomposition of $Cu_3[Cr(SCN)_6]$ and $Cd_3[Cr(SCN)_6]_2 \cdot 8H_2O$ under dynamic conditions, and comparison of their thermal properties with those of previously analysed compounds.

2. Experimental

2.1. Apparatus

The thermal analysis curves of the examined compounds were plotted using a MOM Budapest OD-102/1500°C type derivatograph, in air atmosphere over the temperature range 20–1000°C at a heating rate of 5°C/min. DTA and DTG sensitivities were both 1/10 and TG range was 100 mg. The mass of the samples was 100 mg. α-Al_2O_3 was used as reference material. Samples were run in open, sintered-aluminium oxide crucibles. Diffraction patterns of the initial compounds and their sinters were recorded by means of a Siemens D5000 diffractometer over the 2θ angle range from 2 to 90° with scan step 0.04° and time of scan step 1 s.

2.2. Preparation

Cadmium hexathiocyanatochromate $Cd_3[Cr(SCN)_6]_2 \cdot 8H_2O$ was obtained at room temperature by adding 5% water solution of $K_3[Cr(SCN)_6]$ obtained according to literature [3] to water solution of $Cd(NO_3)_2$. Almost instantly a fine-crystalline pink precipitate was formed.

Copper hexathiocyanatochromate $Cu_3[Cr(SCN)_6]$ was obtained in an analogous way, at room temperature, by adding drop-wise 5% solution of

---

[*] Corresponding author. Tel.: +48-42-6313123.
E-mail address: elaskiba@ck-sg.p.lodz.pl (E. Skiba)

0040-6031/00/$ – see front matter
PII: S0040-6031(00)00487-1

Table 1
Average results of chemical analysis

Compound	Precipitate colour	Outer sphere cation (%)		SCN^- (%)	
		Theoretical	Determined	Theoretical	Determined
$Cd_3[Cr(SCN)_6]_2\cdot 8H_2O$	Purple	26.32	26.33	54.32	54.20
$Cu_3[Cr(SCN)_6]$	Yellow	32.25	32.00	58.95	60.00

$K_3[Cr(SCN)_6]$ to the solution of CuCl acidified with hydrochloric acid. After a certain time, a dark yellow precipitate of the complex copper salt was formed.

The precipitates were filtered off on a hard filter, washed with water and dried in air.

An attempt was made to obtain copper(II) hexathiocyanatochromate using different substrates and various preparation methods. When water solution of $Cu(NO_3)_2$ was used as substrate, a dark yellow precipitate was also formed and a gas with an irritating smell was released from the solution.

Chemical and X-ray analyses showed that in both cases (when either copper(I) or copper(II) salt was used as substrate) $Cu_3[Cr(SCN)_6]$ was formed.

When copper(II) salt was used for synthesis, copper(II) was reduced to copper(I), and thiocyanogen was released from the solution. This process may be explained by the higher redox potential of the Cu^{2+}/Cu^+ system (E^0=0.17 V) than that of the SCN^-/1/2$(SCN)_2$ system (E^0=0.77 V).

Thiocyanate ion in the obtained compounds was determined by the method of oxidation of thiocyanates to sulphates and gravimetric determination of sulphates [4]. Cadmium was determined by complexometric titration in the presence of pyrocatechol violet as indicator [5]. Copper was determined by two methods: extraction-spectrophotometric method with Na-DDTK [6] and spectrophotometric method with PAN [7].

Mean values of the chemical analysis are presented in Table 1. Diffraction patterns of both compounds are presented in Figs. 1 and 2. They explicitly show that the obtained compounds are crystalline. Thermal analysis curves (TG, DTA and DTG) of the compounds under study are presented in Fig. 3.

2.3. Thermal analysis

Thermal decomposition of cadmium hexathiocyanatochromate starts at about 100°C, an endothermic peak observed on the DTA curve at 120°C is connected with a 12% loss in mass. At temperature exceeding 340°C, a very clear 25% loss of the mass of the sample was recorded on the TG curve. A broad exothermic peak appeared on the DTA curve, as a result of overlapping of two exothermic effects, with maxima at 350 and 420°C. A smaller exothermic peak can be observed at 470°C.

Thermal decomposition of copper(I) hexathiocyanatochromate begins at 290°C. A previous slight loss in mass (~2%) at lower temperatures is caused by the drying of the sample.

Over the temperature range 280–460°C, a broad exothermic peak is observed on the DTA curve, accompanied by a considerable loss in mass (25%). As the sample is heated to temperatures over 380°C the mass of the sample increases by 15%.

On further heating (600–800°C), the mass of the sample decreases again. This process is accompanied by very small endothermic peaks on the DTA curve, associated with further decomposition of the sample, which probably proceeds in two stages. Over 800°C, the mass of the sample decreases slightly reaching 45% of the initial mass at the temperature of 1000°C.

2.4. Analysis of thermal decomposition products

In order to investigate the course of the reaction of thermal decomposition, sinters of the salts under study were prepared by heating in air a number of their 100 mg samples in a silite furnace at the rate of 5°C/min up to temperatures determined on the basis of TG curves, corresponding with the end of each stage of decomposition. The sinters in which mass losses were equal or close to those determined from the TG curves were selected for further analyses.

Sinters of $Cd_3[Cr(SCN)_6]_2\cdot 8H_2O$ were prepared at temperatures of 200, 380, 700 and 1000°C, those of $Cu_3[Cr(SCN)_6]$ at 350, 700 and 1000°C. X-ray dif-

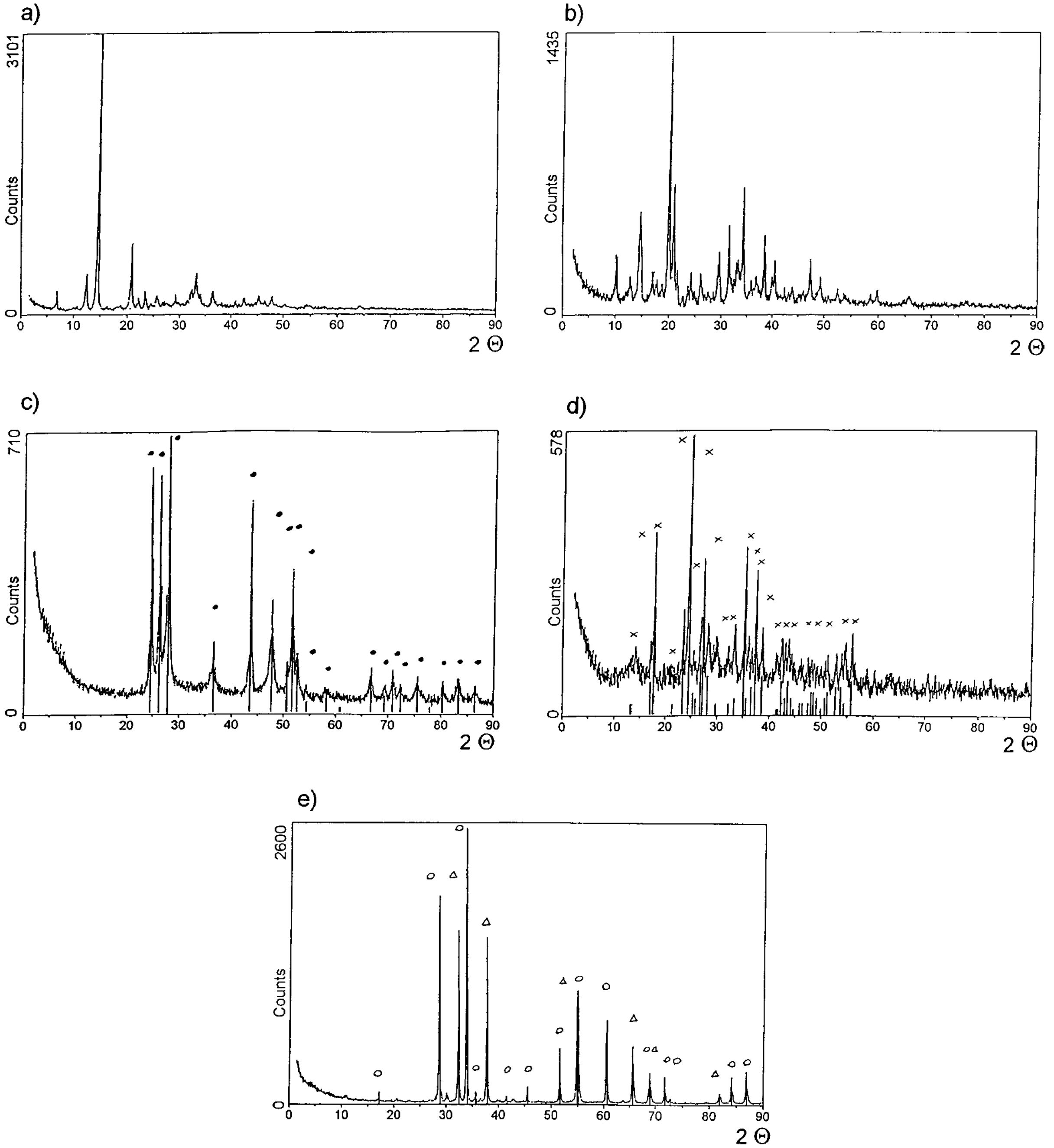

Fig. 1. Diffractions patterns of $Cd_3[Cr(SCN)_6]_2\cdot 8H_2O$ (a) and its sinter at 200°C (b), 380°C (c), 700°C (d), 1000°C (e): (●) CdS; (×) $CdSO_4$; (○) $CdCr_2O_4$; (△) CdO.

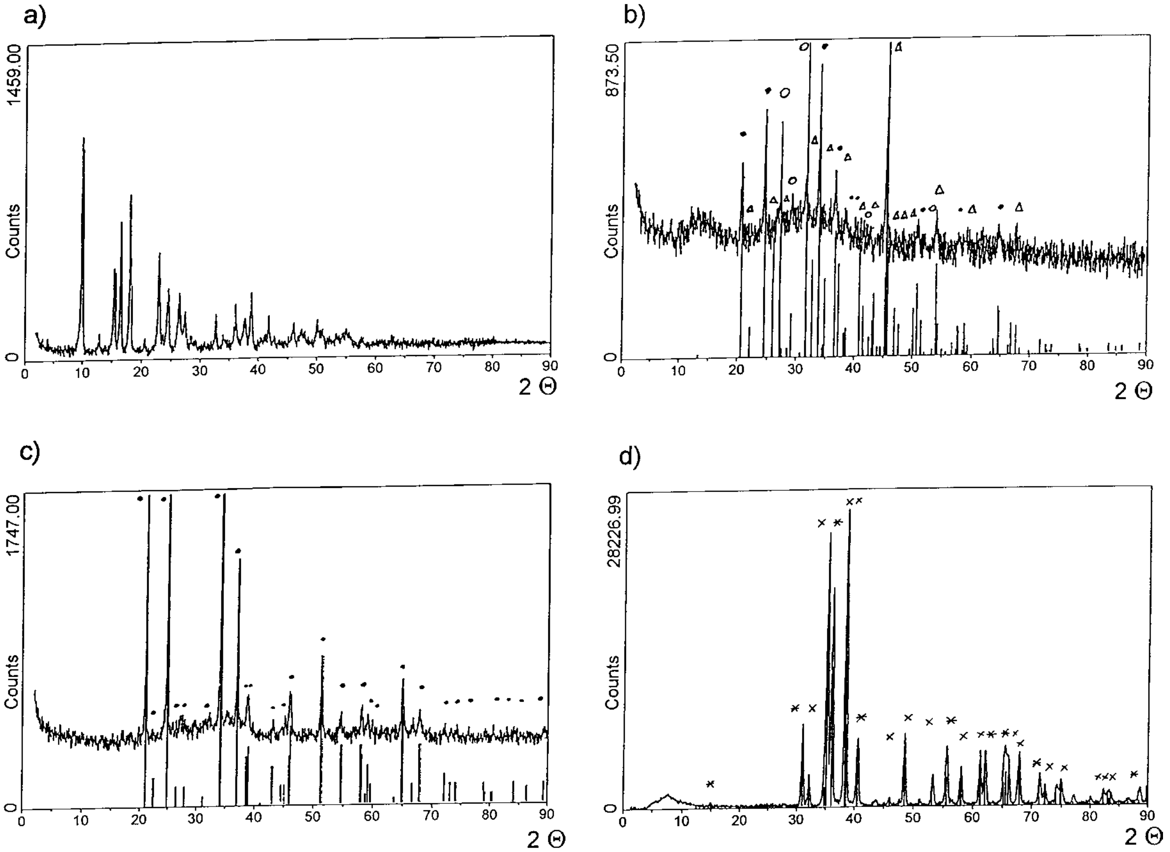

Fig. 2. Diffractions patterns of $Cu_3[Cr(SCN)_6]$ (a) and its sinters at 350°C (b), 480°C (c), 1000°C (d): (×) CuO; (●) $CuSO_4$; (△) Cu_7S_4; (*) $CuCrO_2$; (○) $Cu_{1.8}S$.

fraction patterns of the sinters are presented in Figs. 1(b–e) and 2(b–d).

3. Results

Over the temperature range from 100 to 200°C cadmium hexathiocyanatochromate loses crystallisation water in one stage. The loss in the mass of the sample read from the TG curve is 12%, while that calculated from the formula of the compound is 11%. The 1% difference results from the loss of moisture adsorbed by the sample.

One sharp peak is observed on the DTA curve, which confirms the fact that removal of crystallisation water from the sample is a one-stage process.

Fig. 1b presents the X-ray diffraction pattern of the sinter obtained at 200°C, showing that crystalline $Cd_3[Cr(SCN)_2]$ is an intermediate product of decomposition. A very clear decrease of mass (25%) is observed on the TG curve over 300°C.

Diffraction pattern analysis (Fig. 1c) indicates that a mixture of crystalline CdS with amorphous chromium compounds of unknown composition is the solid intermediate product of decomposition, which is suggested by the high background of the powder diffraction pattern of the sinter produced at this temperature (recorded under the same conditions as in the case of the initial compound).

The overlapping exothermic DTA peaks at temperature range from 340 to 500°C are the effect of simultaneous processes of further decomposition of the compound and decomposition of the cadmium sulphate $CdSO_4$ previously formed. Sharp peaks observed in the diffraction pattern of the sinter

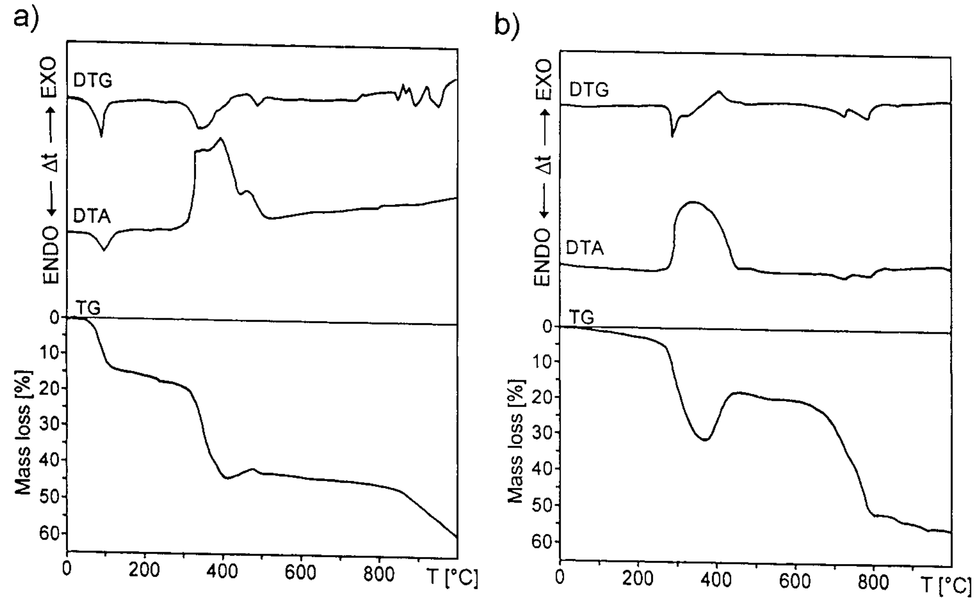

Fig. 3. Thermal decomposition curves of (a) $Cd_3[Cr(SCN)_6]_2{\cdot}8H_2O$ and (b) $Cu_3[Cr(SCN)_6]$.

obtained at 700°C (Fig. 1d) indicate the presence of $CdSO_4$, and the high background should be attributed to the presence of the amorphous chromium compound. In the diffraction pattern of the sinter obtained at 1000°C (Fig. 1e), only sharp peaks corresponding to crystalline CdO and $CdCr_2O_4$ occur.

Thermal decomposition of copper(I) hexathiocyanatochromate starts at 290°C. The TG curve shows a clear mass loss of about 25%, while the DTA curve exhibits a large, blurred exothermic peak whose shape results from overlapping thermal effects of simultaneous processes: a very strong exothermic effect related to oxidation of copper(I) to copper(II) and S^{2-} ions to $SO_4{}^{2-}$ and an endothermic effect connected with the decomposition of the sample. The presence of copper(II) compounds and sulphates was confirmed by diffractometric analysis. Diffraction patterns of the sinters obtained at 350 and 480°C (recorded under the same conditions as those of the initial compound) show high background, which results from the presence of amorphous chromium compounds of unidentified composition in the intermediate products of thermal decomposition of complex salts of cadmium.

Diffractometric analysis of the sinter (Fig. 2b) obtained at 350°C confirmed the presence of crystalline CuS and $CuSO_4$ alongside the above mentioned chromium compounds.

The diffraction pattern of the sinter obtained at 480°C (Fig. 2c) shows maxima, testifying to the presence of crystalline $CuSO_4$, $Cu_2O(SO_4)$ and still amorphous chromium compounds.

When the sample was heated to temperatures over 600°C a mass loss was observed, corresponding with two very small endothermic peaks on the DTA curve, caused by decomposition of $CuSO_4$ to CuO at temperatures over 650°C, which is in accordance with literature data [8]. In the further stage of decomposition (at higher temperatures), recrystallisation of chromium compounds occurs. Therefore, in the sinter obtained at 1000°C (Fig. 2d), a mixture of crystalline CuO and $CuCrO_2$ was identified.

4. Discussion

Cadmium and copper(I) hexathiocyanatochromates(III) of formulae $Cd_3[Cr(SCN)_6]_2{\cdot}8H_2O$ and $Cu_3[Cr(SCN)_6]$, as determined by chemical analyses, separated from mother solutions at room temperature in the form of fine, well formed crystals of characteristic colours.

Thermal decomposition of $Cd_3[Cr(SCN)_6]_2 \cdot 8H_2O$ is a multi-stage process. It starts at lower temperatures (about 100°C) than that of $Cu_3[Cr(SCN)_6]$. It results from the removal of water of crystallisation present in the cadmium salt.

X-ray diffraction analysis showed that the final product of decomposition is a mixture of CdO and $CdCr_2O_4$.

Thermal decomposition of $Cu_3[Cr(SCN)_6]$ begins at 220°C and also proceeds in several stages. Its final product is a mixture of CuO and $CuCrO_2$.

Previous studies and the present work provide evidence that in the group of compounds under investigation, thermal stability, expressed as the temperature of the onset of decomposition, increases in the following order:

$$\begin{aligned} &Pb_3[Cr(SCN)_6]_2 < Hg_3[Cr(SCN)_6]_2 \\ &\quad < Ag_3[Cr(SCN)_6] < Bi[Cr(SCN)_6] \\ &\quad < Cu_3[Cr(SCN)_6] < Tl_3[Cr(SCN)_6] \\ &\quad < Cd_3[Cr(SCN)_6]_2 \end{aligned}$$

For cadmium salt, the temperature of decomposition of anhydrous salt has been assumed to be the decomposition temperature.

Due to the complexity of the thermal decomposition of the compounds under study and the difficulties in obtaining intermediate products of decomposition (overlapping subsequent stages), it is not possible to fully characterise the process of thermal decomposition by giving precise equations representing the occurring processes.

References

[1] B. Ptaszyński, E. Skiba, Thermochim. Acta 217 (1993) 199.

[2] B. Ptaszyński, E. Skiba, Thermochim. Acta 223 (1993) 93.

[3] G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 2, Academic Press, New York, 1965, p. 1374.

[4] G.O. Müller, Praktikum der quantitativen chemischen analyse, S. Hirzel Verlag, Leipzig, 1967, p. 342.

[5] F.J. Welcher, The Analytically Uses of Ethylenediamine Tetraacetic Acid, Van Nostrand, Princeton, NJ, 1958, p. 149.

[6] Kuang Lu Cheng, Roger H. Bray, Anal. Chem. 25 (4) (1953) 655.

[7] A. Cygański, J. Krystek, Chem. Anal. 36 (1991) 769.

[8] C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1953, p. 249.