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Thermal decomposition of metallic diethanoldithiocarbamate complexes

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Abstract

Thermoanalytical study of metallic diethanoldithiocarbamate complexes of the type $M[S_2CN_9C_2H_4OH)_2]_n$, where $M{=}Cd^{2+}$, Cr^{3+}, Mn^{2+} and Bi^{3+}. The thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) techniques were used. The final decomposition products found were metallic sulfides and oxides in nitrogen and air atmosphere, respectively, except for chromium complexes giving up Cr_2O_3 as residue in nitrogen atmosphere. This experimental evidence can be explained by means of a hydroxy complex also formed during the compound synthesis. This was confirmed by means of atomic absorption and TG experiments. The thermoanalytical results give rise to an inference about thermal stability and possible thermal decomposition mechanisms under nitrogen and air dynamic atmospheres. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermoanalytical studies of dithiocarbamates are important to verify its behavior and acting, mainly in industrial and agricultural applications, when they are submitted to conditions of relatively high temperature [1–8].

A dithiocarbamate is the product of the reaction among a primary or secondary amine with the carbon disulfide, in a basic environment. The principal characteristic of dithiocarbamate is its instability in acid environment. In this condition it happens to form the protonated molecule, dithiocarbamic acid. The intermediate decomposition would be in a protonated form with a positive charge density on the atoms of nitrogen and carbon, that produce the N–C bond, that make the dithiocarbamate [9] unstable.

The diethanoldithiocarbamate (DEDC) is the derived dithiocarbamate of the diethanolamine. In its amoniacal form the composition comes in the form of colorless and odorless crystals. Being quite soluble in water it does not prevent melting, with decomposition occurring around 373 K. It presents solubility lightly superior to the other dithiocarbamates, when it forms a complex with metals, due to the presence of the –OH groups of the aminic part. Its apparent stability constant of decomposition in an aqueous media is $k'{=}11.000\ \mathrm{l\ mol^{-1}\ min^{-1}}$, while the necessary pH for a $\tau 1/2{=}10$ h is 7.01.

The present work will accomplish a study of the thermal behavior, using thermogravimetry (TG)

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and differential scanning calorimetry (DSC), in dynamic atmospheres of air and nitrogen of the complexes: $Cd[S_2CN(C_2H_4OH)_2]_2$, $Cr[S_2CN(C_2H_4OH)_2]_3$, $Mn[S_2CN(C_2H_4OH)_2]_2$ and $Bi[S_2CN(C_2H_4OH)_2]_3$.

2. Experimental

2.1. Chemical

All the reagents and solvents: diethanolamine (Merck), carbon disulfide (Merck), ammonium hydroxide (Merck), ethanol (Merck), cadmium chloride (Merck), chromium nitrate (Merck), manganese chloride (Merck), bismuth nitrate (Carlo Erba) and nitric acid (Merck), used were of degree p.a., and were purified.

2.2. Preparations

The diethanoldithiocarbamate, $[S_2CN(C_2H_4OH)_2]^-NH_4^+$, ligand was prepared in an aqueous environment, starting from the reaction between the diethanolamine and the carbon disulfide, second routine is described by Vieira [7]. In an Erlenmayer 9.8 mL (0.100 mol) of diethanolamine was placed, dissolved in 50 mL ethanol, and 7.7 mL (0.100 mol) of concentrated ammonium hydroxide (28%) was added. After addeding slowly under constant agitation under an ice bath, 6.00 mL (0.100 mol) of carbon disulfide was dissolved in 30 mL of ethanol. Complete the addition and agitate the mixture for 30 min, until the formation of a white precipitate, followed by filtration and washing with ethanol. Later on, after crystallization in an ice bath, dissolving the complexing agent precipitated with the smallest possible volume of water (about 50 mL) and afterwards twice the volume was added with ethanol. After recrystallization, the crystals in needle form, were filtered and washed again several times with ethanol portions, dried in vacuum, maintained at low temperature and under protection to avoid exposure to direct light.

The $Cd(DEDC)_2$, $Cr(DEDC)_3$, and $Mn(DEDC)_2$ complexes were obtained stoichiometrically, for direct reactions among $[S_2CN(C_2H_4OH)_2]^-NH_4^+$, and metallic salts soluble in water, except for the reaction of $Bi(DEDC)_3$, which was added slowly to the binder as a function of $Bi(NO_3)_3$ to be amidst acid so that there will not be a fast decomposition of $[S_2CN(C_2H_4OH)_2]^-NH_4^+$, that will result in the formation of the bismuth sulfide (Bi_2S_3). The complexes obtained were isolated, recrystallized from ethanol and dried in vacuo, with yields in the range 70–75%.

2.3. Thermal measurements

For each experiment around 7.00 mg of a recently prepared complex sample was used. The gas flow was controlled with the rate around 200 mL min^{-1}. The air used, coming from a compressor, was filtered and dried through a cooler unit Norgren Martonair, model D10200.0010. In all the experiments a heating rate of 283 K min^{-1} was used. The thermogravimetric DuPont model TGA-951, coupled to a thermal analyzer DuPont Series 9900 and equipped with a recording HP model 7440A was used.

In the experiments DSC techniques were used with around 6.00 mg of sample. In this case a closed aluminum vessel with covers were used, with a perforation in the center of the cover to eliminate the gases generated during the process. The flow of the gas was controlled using a rate of 200 mL min^{-1}.

In all the experiments a rate of heating of 283 K min^{-1} was used. In the case of bismuth a rate of heating of 293 K min^{-1} was also used, in atmospheric air, to evidence an inflection that appears around 473 K.

A differential scanning calorimetric DuPont model DSC 910, coupled to a thermal analyzer DuPont Series 9900, equipped with a HP model 7440A recording was used.

2.4. Other measurements

An X-ray Siemens model D-5000 diffractor, an electrothermal device to determine the melting point of the sample, an Intralab model AA12/1475 spectrophotometer, equipped with an air/acetylene or nitrous air/oxide flame and an FTIR Nicolet model 5SXC, equipped with a TGS detector in the strip of 4000–400 cm^{-1} were used; the spectra were obtained with KBr tablets.

3. Results and discussion

The reaction products between the metallic ions and diethanoldithiocarbamate, $[S_2CN(C_2H_4OH)_2]^-$

Table 1
Results of the characterization of the complexes: colors, melting points (MP), temperature intervals/TG, mass percentege and FTIR bands

Compound	Color	MP (°C)	Inteval temperature TG (°C)	Mass percentage (μg l^{-1})		FTIR bands (cm^{-1})		
				T	*P*	C=S	N–CS	C–N
Cd(DEDC)$_2$	White	153[a]	121–900	1.00	0.98±0.04	984	1410	1486
Cr(DEDC)$_3$	Gray	190[a]	50–900	6.68	6.31±0.09	991	1416	1483
Mn(DEDC)$_2$	Black	143[a]	110–900	3.00	2.91±0.01	981	1418	1486
Bi(DEDC)$_3$	Yellow	180[a]	124–900			971	1418	1489

[a] With decomposition.

(DEDC), produce compounds with different colorations, as shown in Table 1. The melting points will occur with decomposition, as listed in Table 1. The FTIR results are presented in Table 1, and are coincident with that mentioned in the literature [9–11]. The spectra suggest absorption in the region of 3500–3000 cm^{-1}, with regard to the OH group. We cannot affirm that hydration waters are due to the presence of this group in the diethanolamine molecule. The results of absorption atomic analysis are listed in Table 1.

3.1. Diethanoldithiocarbamate of cadmium(II)

The TG curve in nitrogen atmosphere is presented in Fig. 1. This curve exhibits that the thermal decomposition of the compound occurs in a stage between 394 and 652 K, with loss of mass of 67.68%, resulting in a yellow residue with 32.32% of the initial mass (theoretical for CdS=30.54%). In the presence of concentrated HCl a precipitate of white coloration was formed, related to the decomposition of DEDC, that can form diethanolammonium chloridrate in the presence of HCl, with the intention that there should be no crystallization water in the complex. The yellow residue is probably the sulfate of cadmium, due to the color [12] and odor of sulfide gas in the presence of HCl. X-ray has confirmed the presence of CdS as a main phase of the residue and presence of small amounts of oxides and cadmium oxysulfates, probably formed with oxygen present in the nitrogen. The presence of these oxysulfates explains the difference in the composition between the theoretical and experimental residues.

Fig. 2 presents the DSC curve in nitrogen atmosphere. In this curve three peaks relative to the endothermics were observed to that of the thermal events involving the composition. In the first two peaks at 435.5 and 455.3 K, the decomposition of

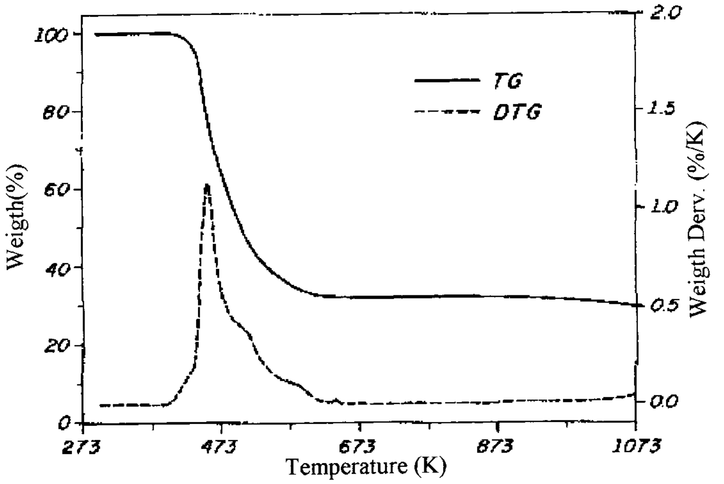

Fig. 1. TG/DTG curves in nitrogen atmosphere of diethanoldithiocarbamate of cadmium(II).

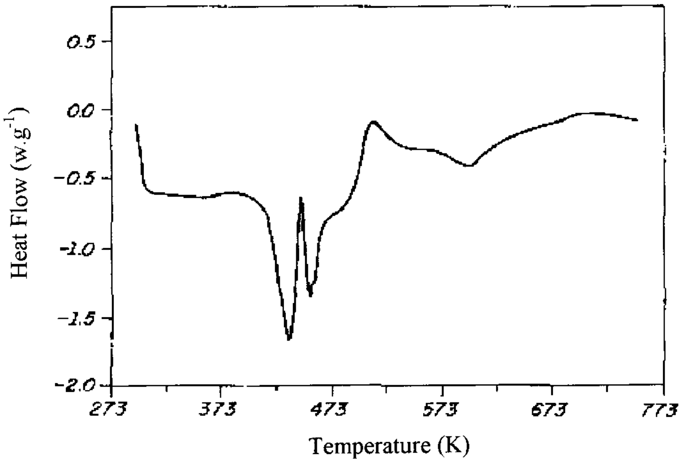

Fig. 2. DSC curve in nitrogen atmosphere of diethanoldithiocarbamate of cadmium(II).

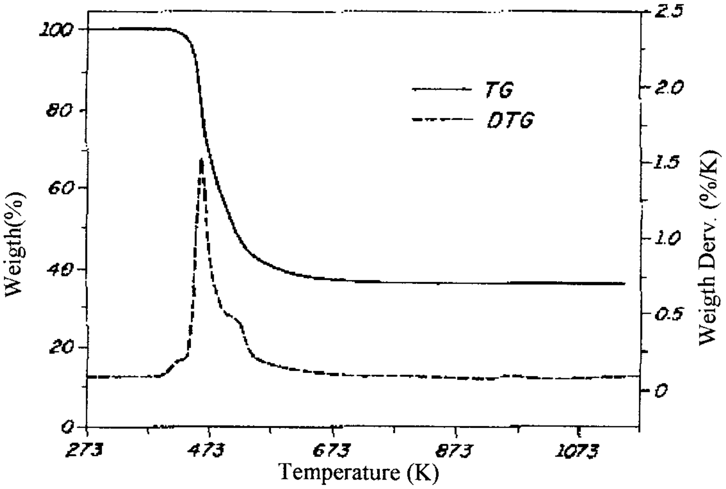

Fig. 3. TG/DTG curves in air atmosphere of diethanoldithiocarbamate of cadmium(II).

DEDC occurred and the third peak at 625.2 K, was attributed to the residual sulfur burnt to form cadmium sulfide. The study made in a glass tube, showed that at the temperature of the first peak melting of the complex, as well as, condensation of water in the wall of the tube during the experiment did not occur.

Curved TG in air atmosphere is presented in Fig. 3. This curve shows that the decomposition occurs in a similar way to that of the nitrogen, with only loss of mass of 65.44%, and residue of the order of 34.86%. In this residue the cadmium sulfide prevails seemingly, according to experiment mentioned previously. The content, lightly superior to the theoretical one, will be 30.55%, is probably due to the presence of sulfur and organic material.

DSC curve in air atmosphere is presented in Fig. 4. It also presents two endothermic peaks at 434.2 and 458.0 K, referring to the decomposition of the complex. The exothermic peak for 707.4 K is related to the organic residue burn due to the oxygen present in the nitrogen, the second hypothesis being more probable in the function of the relative increase of energy to the peak in the air atmosphere, in relation to the experiment fact under inert atmosphere of nitrogen.

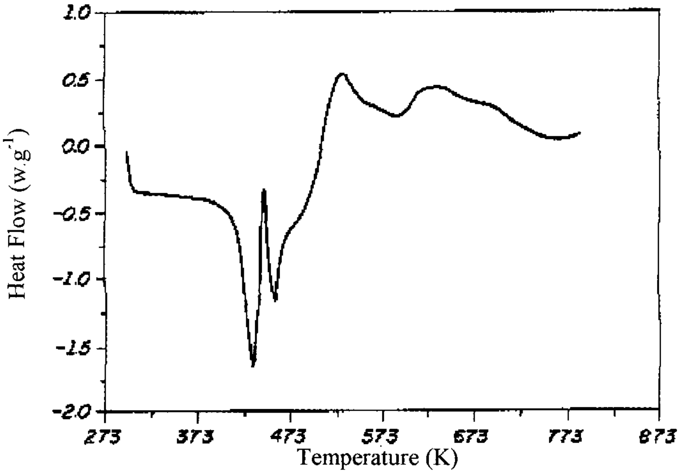

Fig. 4. DSC curve in air atmosphere of diethanoldithiocarbamate of cadmium(II).

3.2. Diethanoldithiocarbamate of chromium(III)

The TG curve, in nitrogen atmosphere, was expected to have Cr_2S_3 as a residual product. But the experimental residue was of the order of 37.19% (theoretical=16.88%), from the complexes $Cr(DEDC)_3{\cdot}4H_2O$. The presence of the molecules of water hydration was considered initially based on the mass loss of about 322.6–384.0 K. However, diffraction studies of X-ray applied in the residues, obtained at 973.0 K, show the presence of Cr_2O_3. New studies using supra-pure and ultra-pure nitrogen and helium were used. In all the experiments an alteration in the X-ray diffraction results, that confirm the presence of Cr_2O_3 (eskolaite phase), were not obtained.

Besides these studies a test was made in an open tube made of glass in a liquid vaseline bath at 473.0 K, which shows the presence of water in the compound. However, to have this correlation between the grade of obtained residue and the starting compound, it is supposed that the last one presents a molecular mass of the order of 450–470 g mol^{-1}. It is necessary to suppose a compound which has Cr^{2+} that would be formed by reduction of the metal during the synthesis for the above explanation to be true. This kind of reduction process generating a compound of the type $Cr(DTC)_2$, was related by Fackler and Holah [12], to produce unstable compounds and the environment containing NO^{3-} of the starting salt $Cr(NO_3)_3$ which is an oxidizer and does not favor the reduction process Cr(III)→Cr(II).

An additional information for elucidation of these facts is the result of the studies of atomic absorption that present a chromium grade of 8.96%. This proportion associated to the high content of the obtained residue and associated to the results of X-ray diffraction, suggest the formation of a polymeric compound, as described by Åkerstrom [13], that proposed polymeric structures for several DTC of copper. This hypothesis is compatible with the formation of the Cr_2O_3, because the metal reacts more easily with oxygen than sulfur [14] and the synthesis is made adding solution containing the binding in an alkaline environment (pH=9 to the solution of the metal in pH=4). So, when this mixture is produced, it is possible to have a micro region, where the pH is superior at the pH of the chromium hydrolysis, that favors the appearance of the anhydro hydroxy complex.

The chromium bonding with the group –OH of the adjacent amines completes the hexacoordination, that is frequent in the complexes of this metal [14].

The difference between the theoretical residue to that of the present structure (28.54%) and the experimental residue (37.19%) was attributed to the presence of carbonized residue that was confirmed when burnt in mufla at 1173.0 K for 2 h, under air-flow around 8%.

The experimental residue of Cr_2O_3, was 29.19% while the theoretical would be 28.54%. The TG curve in air follows similar paths as nitrogen with regard to the temperatures and the amounts of loss of mass in each stage, except the abrupt loss of mass around 573–623 K, occurs in air evidencing that the organic material burns in the presence of oxygen.

Qualitatively the mass losses around 318–423 K would be relative to the mass losses for decomposition of dithiocarbamate, due to the weak S–Cr bond, followed by a possible intramolecular dehydration around 423–523 K, evidenced by the experiment in a glass tube opened in a liquid vaseline bath. Finally, the decomposition of the remaining material occurs generating Cr_2O_3 and carbon.

The DSC curves, in nitrogen, in which an endothermic process is observed around 348–423 K, are attributed to the decomposition of diethanoldithiocarbamate. Subsequently an endothermic process related with an intramolecular dehydration is observed around 459–483 K, being followed by a slow endothermic decomposition, until the end of the experiment.

The DSC curve is an experiment performed in atmospheric air, in which the same endothermic peak is observed around 348–423 K, following an endothermic/exothermic process. The endothermic process, attributed to the elimination of the molecules of water intramolecules, was shown by DSC experiments with a scanning speed of 293 K min^{-1}.

3.3. Diethanoldithiocarbamate of manganese(II)

The TG curves in nitrogen atmosphere were considered to decompose in two stages. In the beginning the simultaneous occurrence of the processes makes the determination of the initial and final temperatures difficult. The first step occurred between 498.0 and 537.0 K, where 91.04% of the initial mass was lost, resulting in a residue of 18.96%, in this temperature. This residue was attributed to the presence of MnS (theoretical=20.94%). This residue is thermally stable up to 950.0 K. The second stage begins at 950 and extends up to 1026.0 K, when the residue is 15.83%, indicating a reduction process to metallic Mn (theoretical=13.22%). The residues were studied using X-ray at 633.0 and 1073.0 K and the results show the presence of metallic Mn.

The DSC curves in nitrogen atmosphere, show a decomposition peak, with an area proportional to 54.4 J g^{-1}, in 438.7 K, that was not attributed to the melting, because in this temperature a significant mass loss already occurs, according to the TG curves.

Soon after a new endothermic peak appears at 443.4°C, also associated with the decomposition of the complex. The presence of this peak evidences the decomposition in more than a step, maybe by thiocyanate, according to the TG experiment.

The TG curves, in air atmosphere, show that the decomposition occurs in three steps. The first step occurs between 383.0 and 571.0 K. In this temperature the residue can be $MnSO_4$, containing 35.98% of the initial mass (theoretical=36.34%). The second step occurs between 571.0 and 882.0 K, being proportional to the decomposition of the sulfate, generating MnO_2 or MnS, since the two compositions present very close molecular weights. The atmosphere composed of air suggests the presence of the oxide in preference to the sulfide. For 882.0 K the experimental residue was 22.67% (theoretical=20.92% for MnO_2 or MnS). The MnO_2 was confirmed by X-ray diffraction. The last transition occurs between 946 and 1068 K, with a loss of 5.99% of the initial mass, generating an experimental residue of 16.75% that corresponds to Mn_2O_3 (theoretical=19.00%), confirmed by X-ray diffraction.

The DSC curve in air atmosphere, shows endothermic peaks at 391.41 and 414.03 K (at that temperature a sulfide-like smell was observed in the experiment with the capillary) and exothermic peaks at 384.27, 430.69 and 466.41 K were attributed to the decomposition of the binding. Exothermic peaks were also observed at 571.00 and 864.03 K, which were attributed to the oxidation of the metallic residue generating $MnSO_4$.

3.4. Diethanoldithiocarbamate of bismuth(III)

For the TG curves in nitrogen, the decomposition of the complex occurs in a single transition between 397.0 and 949.0 K, with a loss of mass of 65.15%.

The residue of 35.44% was attributed to the Bi_2S_3 (theoretical=34.28%); confirmed by X-ray. After the formation of the Bi_2S_3, above 973.0 K a slight mass gain due to the probable oxidation of the oxysulfate, due to contamination with O_2, in the nitrogen used was noticed. It was also observed that the support sample used, composed of platinum, presents indications of corrosive attack when the sample is warm at temperatures around 1073.0 K. This was attributed to the presence of the sulfur that attacks the platinum in high temperatures.

The DTG curves show that the decomposition has intermediate steps difficult to be attributed to by virtue of the simultaneous occurrence of the processes, that makes the choice of the points to execute the stoichiometric calculation difficult. Speculative studies with the mass losses suggest a decomposition pathway through formation of the morpholinodithiocarbamate.

The DSC curve in nitrogen atmosphere that presents endothermic peaks at 411.70 K was not attributed to the melting due to the mass loss occurred at this temperature. Two exothermic peaks appear at 423.0 and 553.0 K, relative to the decomposition of the complex.

The TG curves in air atmosphere are similar to the nitrogen, but present temperatures lightly superior to the transitions. The residue in air does not present a definite stoichiometry. It could be a mixture composed of Bi_2S_3 (theoretical=34.28%); $Bi_2(SO_4)_3$ (theoretical=47.09%), with an experimental grade of 40.42% in 904.0 K.

The DSC curves in air atmosphere show endothermic peaks at 411.70 K, also not attributed to the melting; exothermic decomposition peaks at 512.89, 564.08 and 704.55 K and an exothermic peak due to the oxidation of metallic residue at 800.98 K, to the formation of the mixture composed by bismuth sulfide/sulfate.

4. Conclusion

The thermal studies developed in the present work, demonstrate the obtainment of: Bi_2S_3, CdS, MnS in nitrogen atmosphere. In atmosphere composed of air the following oxides were obtained: Bi_2O_3, Mn_2O_3, and the cadmium generated as residue was CdS, with a small portion of CdO and oxysulfate according to the results of X-ray diffraction. In the case of the chromium complexes, the presence of Cr_2O_3 as residue in both the atmosphere, as well as the analysis for atomic absorption of the grade of metal of the original complex conducted led to the proposition that this would be a hydroxy complex.

It is important to observe that several subsequent steps appear in the DTG curves, showing that the mechanisms of thermal decomposition, mainly bismuth and manganese, occur by relatively complex processes. The transitions that occur simultaneously did not allow the stoichiometric calculations to define the intermediates formed during the steps, under the experimental conditions used.

As an example, the presence of intermediates as the metallic thiocyanates, proposed by Sharma [5], as a pathway to the decomposition to the dithiocarbamates was not verified.

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