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INITIAL MASS LOSS IN ANHYDROUS MANGANESE(II) PYRROLIDINEDITHIOCARBAMATE
Decomposition or sublimation

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Abstract

Investigation on the nature of an initial mass loss observed for Mn(II) pyrrolidinedithiocarbamate complex is described. No evidences of decomposition are observed in infrared or mass spectra, elemental analysis and scanning electron microscopy of the residue at the end of the first thermal event, when compared with the same data for the original complex. Partial sublimation is assigned as the physical event after several experiments. The results are comparable with the findings for other complexes of the first transition series with pirrolidinedithiocarbamate.

Keywords: pyrrolidinedithiocarbamates, sublimation, thermogravimetry

Introduction

Dithiocarbamates (DTC) present countless applications such as rubber vulcanization accelerators [1]; fungicides and bactericides in the agriculture [2]; coadjutant in the tuberculosis, AIDS and cancer treatment [3]; as complexing agents for different metals in several analytical determinations and intermediates of organic syntheses. The knowledge of the thermal properties is fundamental as complementary information to obtain the maximum utilization mainly in industrial applications.

The dithiocarbamates are products derived from aliphatic or cyclic amines and carbon disulfide. The reason for studying these cyclic DTC derivatives is due, mainly, to the fact that they are thermally more stable than the aliphatic analogues [4]. It was verified, in a comparative study, that DTC derived from the five-membered amminic ring pyrrolidine behaves completely different than the similar six-membered DTC derived from the piperidine, an other cyclic amine [4].

In this work, manganese(II) pyrrolidinedithiocarbamate ($MnPyr_2$) was synthesized from anhydrous media. Its TG curve revealed the occurrence of an initial mass

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loss that cannot be attributed to the loss of residual solvent and it does not present stoichiometric correlation with a decomposition process. The results of TG were complemented with DSC, elemental analysis, mass spectral analysis, IR spectroscopy, scanning electron microscopy data and visual tests. The information from all these techniques was compared with the same data of the original complex and the product formed after such a mass loss.

Experimental

Ammonium pyrrolidinedithiocarbamate (NH_4Pyr) was prepared according to a procedure earlier described [4], recrystallized from ethanol–water 1:1 (v/v) and then dried in a vacuum oven at 40°C, for 12 h.

$MnCl_2{\cdot}2H_2O$ was dehydrated according to the procedure described by Pray [5], using thionyl chloride. The metallic complexes were obtained by direct reaction of the previously dehydrated $MnCl_2$ and NH_4Pyr dissolved in isopropanol dried and purified in agreement with Perrin and Armarego [6]. The reaction was performed in a glove-bag, under nitrogen atmosphere. The resulting precipitates were filtered, washed with isopropanol and dried in a vacuum oven at 40°C, for 12 h.

The characterization of the complexes was performed by elemental analysis, IR spectroscopy and flame atomic absorption spectroscopy. For the residue in the sample holder after the thermal event elemental analysis, IR spectroscopy, mass spectral analysis, scanning electron microscopy and visual tests were used.

TG curves were obtained in a TGA-2050 module coupled to a TGA-2100 thermal analyser (TA Instruments), using sample of ca. 7 mg, heating rate of 10°C min^{-1}, under a nitrogen gas flow of 90 mL min^{-1} in an Al_2O_3 sample holder. DSC curves were recorded in a TGA-951 differential scanning calorimetric module coupled to a TGA-2100 thermal analyser (TA Instruments), using sample of ca. 5 mg, heating rate of 10°C min^{-1}, in a covered aluminum sample holder, under a nitrogen gas flow of 90 mL min^{-1}.

Results and discussion

Under nitrogen atmosphere the TG curve (Fig. 1a) showed an initial mass loss between 67–236°C, equivalent to 10.1% of the initial sample mass. The DTG curve evidences two peaks at 150 and 220°C, while DSC (Fig. 1b) presents two endothermic peaks at 112.7 and 222.1°C, corresponding to these processes.

A decomposition process would implicate in a change in the spectral shape of the IR spectra and in the elemental composition of the product formed in relation to the original complex. A sublimation process should occur, usually, by total mass loss, based on the vapor pressure of the material. However, in the present case, only part of the mass was lost.

In the sense of characterizing the product obtained at about 240°C, initially elemental analysis was performed, the results are presented in Table 1, compared with the results obtained for the original complex. It is concluded from these results that

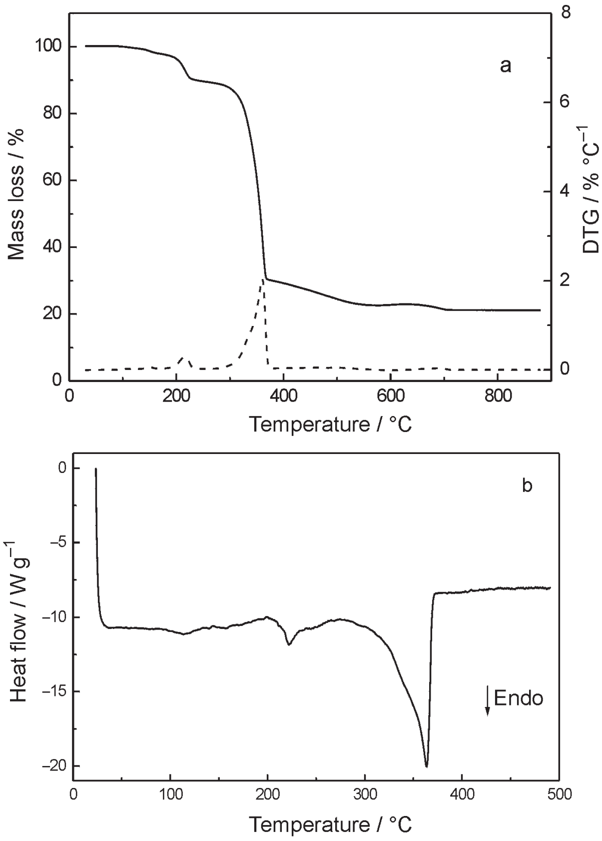


Fig. 1 TG, DTG (a) and DSC (b) curves for the $MnPyr_2$

there was no significant variation in the elemental composition, in spite of the loss of 10.1% of the original complex mass.

Table 1 Analytical data for the original complex ($MnPyr_2$) and the product at 240°C

Compound	Element/%		
	C	N	H
$MnPyr_2$ (calc.)	34.6	8.1	4.6
$MnPyr_2$	34.1	8.1	4.8
$MnPyr_2$ 240	35.1	7.8	4.8

The IR spectra of the original complex in comparison with the residues obtained after dynamic heating (10°C min^{-1}) at about 240°C, are presented in Fig. 2.

Regarding the dynamic heating, it can be affirmed that there was no significant alteration in the spectral shape, in accordance with the elemental analysis results.

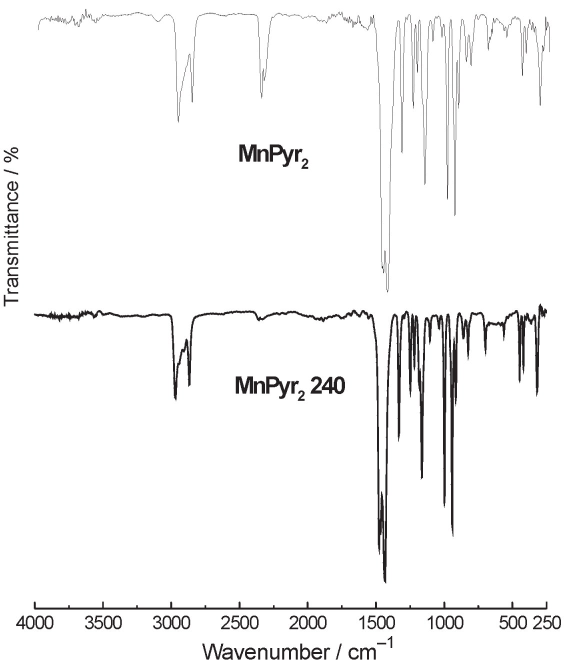
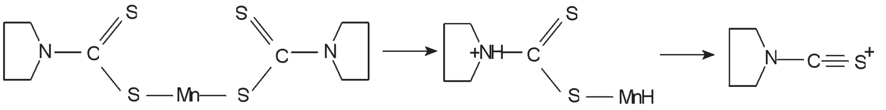


Fig. 2 Comparison of IR spectra of original complex (MnPyr$_2$) and the product obtained after heating at 240°C (MnPyr$_2$ 240)

In addition to the previous experiments, mass spectra of the original complex and of the residue of dynamic heating at about 240°C were obtained, for better understanding of the thermal event. Still in this case, the fragmentation is the same for both samples. The main peaks were observed in *m*/*z*=347.5 (molecular ion); 203 and 114. These results are in agreement with those described by Dias *et al.* [7] for the following fragmentation:



The complex was also heated under nitrogen flow in a glass tube (20×2 cm), in a glycerine bath at about 240°C. IR data of the condensed data also showed the presence of the original complex.

Finally, the original complex and the residue obtained at about 240°C were analyzed by mean of scanning electron microscopy, as shown in Fig. 3.

These micrographs suggest a change in the surface of the crystals, without structural modification, thus avoiding the total sublimation of the complex.

The characterization of the material present in the sample holder after heating at 240°C, by the techniques mentioned above, revealed that the degradation of the com-

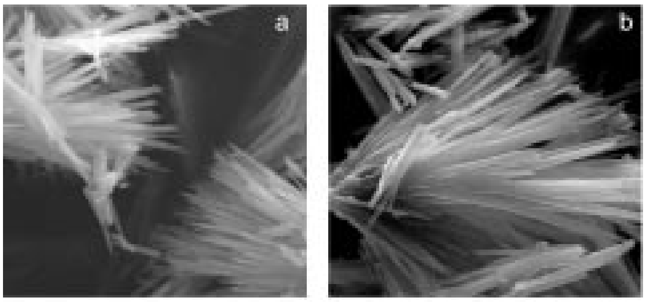


Fig. 3 Scanning electron microscopy of $MnPyr_2$ (a) and the product obtained after heating at 240°C (b) $MnPyr_2$ 240, under magnification of 3000×SE

plex did not take place up to this temperature and that the initial mass loss is due to a volatilization process of the complex.

Under dynamic heating the complex decomposition takes place between 236–707°C, resulting in a 21.2% final product attributed to MnS (calc.=22.4%).

Evidences of the same phenomenon were verified for all the anhydrous Pyr complexes of the first transition series, being mostly remarked for $MnPyr_2$.

Conclusions

From the results presented above it is possible to conclude that the initial mass loss do not represent the decomposition of the complex and was attributed to volatilization of the solid.

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