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Differences in thermal decomposition of Ag(I), Mn(II), Fe(II) and Fe(III) complexes of cyclic dithiocarbamates

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Abstract

The thermal decomposition of pyrrolidinedithiocarbamate (Pyr) and piperidinedithiocarbamate (Pip) complexes of Ag(I), Mn(II), Fe(II) and Fe(III) have been investigated by thermogravimetry and differential scanning calorimetry. The decomposition intermediates and final products were identified from their X-ray diffraction patterns. Changes in their IR spectra were correlated with their thermogravimetric profiles. The hydrated compounds decomposed without loss of water and oxides were detected as the final decomposition products even in nitrogen atmosphere. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pyrrolidinedithiocarbamates; Piperidinedithiocarbamates; Dehydration; Decomposition

1. Introduction

Dithiocarbamates (DTC) are products of the reaction between carbon dissulphide and primary or secondary amines in basic medium. Their properties and applications have been reported in several papers and reviews [1–10]. Presently, the interest in the stability of these compounds has been renewed with the utilisation of DTC as coadjuvant in AIDS treatment [11,12]. In the past, they have also been proposed for tuberculosis [13] and cancer [14] treatment. Thermoanalytical data are important when related to the industrial application of such compounds [1,2,5,10].

Recently, we presented data about the influence of the aminic substituent on the thermal stability of cyclic DTC [15–17]. In this work, the thermal decomposition of pyrrolidinedithiocarbamate (Pyr) and piperidinedithiocarbamate (Pip) complexes of Ag(I), Mn(II), Fe(II) and Fe(III), were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) in order to complete the earlier studies. The thermoanalytical results were correlated with infrared spectroscopy (IR) and X-ray diffraction (XRD) data in order to evaluate the differences caused by the presence of different heterocyclic amines in the ligand.

2. Experimental

2.1. Synthesis of the ligands and complexes

The ammonium salts of the dithiocarbamates were prepared by direct reaction between piperidine or pyrrolidine and CS_2 in the presence of stoichiometric amount of ammonium hydroxide. They were

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recrystallised from acetone (NH_4Pip) or ethanol-water 1:1 (v/v) (NH_4Pyr) and dried in a vacuum oven at 50°C for 8 h [15,16]. The complexes were obtained by direct reaction of the DTC ammonium salt and $AgNO_3$, $MnCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$ or $NH_4Fe(SO_4)_2$ [15,16]. The resulting precipitates were filtered off, washed with acetone and dried as above.

2.2. Equipment

The compounds were characterised by IR spectroscopy (KBr pellets) on a Bomen MB-102-FTIR spectrophotometer. Metals were assigned by flame atomic absorption spectroscopy on an Intralab AA12/1475 (Gemini) spectrophotometer except for silver, which was determined by potentiometric titration with NaCl. The C, H and N contents were determined by elemental analysis using a Fisons EA 1108 CNHS-O instrument.

The TG curves were recorded on a DuPont 2100 thermoanalyser coupled to a TGA 2050 thermogravimetric module under a gas flow of 90 ml min^{-1} (N_2 or air), in a Pt crucible, at 10°C min^{-1} heating rate and using samples of about 7 mg of each compound at atmospheric pressure. The DSC curves were recorded on a DuPont 9900 thermoanalyser coupled with a DSC 910 calorimetric module under a gas flow of 90 ml min^{-1} (N_2 or air), in aluminium hermetic pans, at 10°C min^{-1} heating rate and using samples of about 5 mg of each compound at atmospheric pressure. The DSC cell was calibrated using In metal (>99.9%) as standard for temperature and energy. The X-ray diffraction patterns were obtained on a Siemens D-5000 diffractometer.

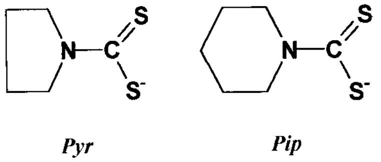

Fig. 1. Structural formulae for the ligands.

3. Results and discussion

The structural formulae of the ligands are shown in Fig. 1. The prepared compounds are listed in Table 1 and the formulae given are in agreement with the elemental analysis. The iron(II and III) complexes of Pip and Pyr showed one hydration water molecule while silver and manganese complexes and ammonium salts were anhydrous. The IR data shown in Table 1 suggest that in the Pyr complex, the ligand is bidentate, represented by the single strong band in 980–1050 cm^{-1} region [2,18], except for the silver complex and the ammonium salts where, a doublet appears in this region. All the Pip complexes exhibit split peaks in the same region suggesting monodentate character [2,18]. These differences are closely related to the behaviour of the TG/DTG and DSC curves (see below).

Table 1
Analytical and IR spectral data for the compounds

Compound	Found (calculated) (%)				IR (cm^{-1})[a]		
	Metal	C	H	N	ν (C=S)	ν (M–S)	ν (C–N)
NH_4Pyr	–	36.6 (36.6)	7.5 (7.4)	16.8 (17.0)	993, 971	1117	1400
AgPyr	42.1 (42.5)	23.3 (23.6)	3.2 (3.2)	5.9 (5.5)	998, 1010	328	1474 (1425)[d]
$MnPyr_2$	16.0 (15.8)	33.8 (34.6)	4.6 (4.6)	8.1 (8.1)	997 (980)[c]	318 (385)[b]	1478 (1450)[c]
$FePyr_2{\cdot}H_2O$	15.5 (15.2)	32.7 (32.8)	4.8 (5.0)	8.0 (7.7)	1000	324	1482
$FePyr_3{\cdot}H_2O$	11.0 (10.9)	35.8 (35.2)	5.1 (5.1)	8.7 (8.2)	999 (1000)[b]	322 (347)[b]	1488 (1460)[b]
NH_4Pip	–	40.8 (40.4)	8.0 (7.9)	14.3 (15.7)	993	–	1409
AgPip	40.1 (40.2)	26.3 (26.9)	3.4 (3.8)	5.1 (5.2)	1007, 950	328	1480
$MnPip_2$	14.0 (14.6)	37.8 (38.4)	5.4 (5.4)	7.3 (7.5)	1005, 950	366	1480
$FePip_2{\cdot}H_2O$	14.1 (14.2)	36.5 (36.5)	5.3 (5.6)	7.0 (7.1)	1000, 975	329	1482
$FePip_3{\cdot}H_2O$	10.2 (10.1)	38.7 (39.0)	5.5 (5.8)	7.3 (7.6)	999, 941	331	1489

[a] Literature values in parentheses;
[b] Ref. [22]; [c] ref. [23]; [d] ref. [24].

Table 2
TG (residues and temperature range) and DSC data corresponding to the decomposition of the Pyr compounds

Process	Temperature range (°C)	Residue (%)		DSC data[a], peak temperature (°C)
		TG	Calculated	
N_2 atmosphere				
AgPyr → Ag_2S	130–438	51.6	48.8	307 (endo)
$MnPyr_2$ → MnS	196–>800	26.1	25.5	363 (endo)
$FePyr_2{\cdot}H_2O$ → FeO	88–352	29.1	19.6	206, 253, 302, 336 (endo)
FeO → Fe_2O_3	353–>800	19.8	21.8	457 (endo)
$FePyr_3{\cdot}H_2O$ → Fe_2O_3	114–850	15.1	15.6	125–200–210–240–260 (endo)
Air atmosphere				
AgPyr → Ag_2S + Ag	107–348	41.9	–	133 (exo), 173 (exo)
Ag_2S → Ag_2SO_4	438–555	43.9	–	311 (endo), 330 (exo)
Ag_2SO_4 → Ag	776–868	38.8	42.5	–
$MnPyr_2$ → $MnSO_4$	189–390	43.2	43.1	150–250 (endo)
$MnSO_4$ → Mn_2O_3 + $MnSO_4$	420–570	35.0	–	515 (exo)
Mn_2O_3 + $MnSO_4$ → Mn_2O_3	>800	23.6	22.7	–
$FePyr_2{\cdot}H_2O$ → Fe_2O_3	110–>800	19.6	21.8	211, 289, 439 (exo)
$FePyr_3{\cdot}H_2O$ → Fe_2O_3	135–620	15.1	15.6	125 (endo)

[a] Exo: exothermic process; endo: endothermic process.

3.1. Thermal decomposition of the Pyr complexes

The mass losses, temperature ranges and final decomposition products for Pyr complexes are presented in Table 2. The products formed in each step are proposed on the basis of their X-ray diffraction patterns. The TG/DTG and DSC curves are presented in Fig. 2 (under nitrogen) and Fig. 3 (under air).

Under nitrogen atmosphere, the silver complex decomposed in a single step, suggesting the formation of metallic sulphites. Under air the decomposition is via the sequence Ag_2S, Ag_2SO_4, Ag. The final product was metallic silver.

Under air, the manganese complex presented a mass gain, probably due to the oxidation of the metal centre and Mn_2O_3 and $MnSO_4$ as decomposition products according to XRD data. Two steps of decomposition were observed under nitrogen.

Fe(II) and Fe(III) complexes decomposed slowly without dehydration and the oxygen atom was retained to form Fe_2O_3 as final product in both air and nitrogen atmospheres. Similar results were observed for Cr/bis-2-hydroxyethyldithiocarbamate (DEDC) complex [19]. Before decomposition the $Fe(Pyr)_3$ presented reduction to $Fe(Pyr)_2$, since similar TG/DTG and DSC curves were observed in both cases. This reduction has been previously observed in solution containing Fe(III)/DEDC complex [20].

The DSC curves showed good agreement with the observations in the TG/DTG data (Table 2). Some peaks without correspondent mass change are described below.

A sharp endothermic peak is present in the $FePyr_3$ curve around 125°C in both atmospheres, giving evidence of the reduction in the metal centre. After this temperature, the DSC curves presented similar profiles. The endothermic peak at 133°C observed under air for $MnPyr_2$ has been attributed to structural changes in the complex since there is no mass changes or melting process observed at this temperature. Under air, the oxidation of the metal masks this peak.

3.2. Thermal decomposition of the Pip complexes

The mass losses, percentage of residues, temperature ranges and final decomposition products, observed in each step of TG/DTG curves for Pip complexes are given in Table 3. The intermediates are proposed on the basis of their X-ray diffraction patterns. The TG/DTG and DSC curves are presented in Fig. 4 (under nitrogen) and Fig. 5 (under air).

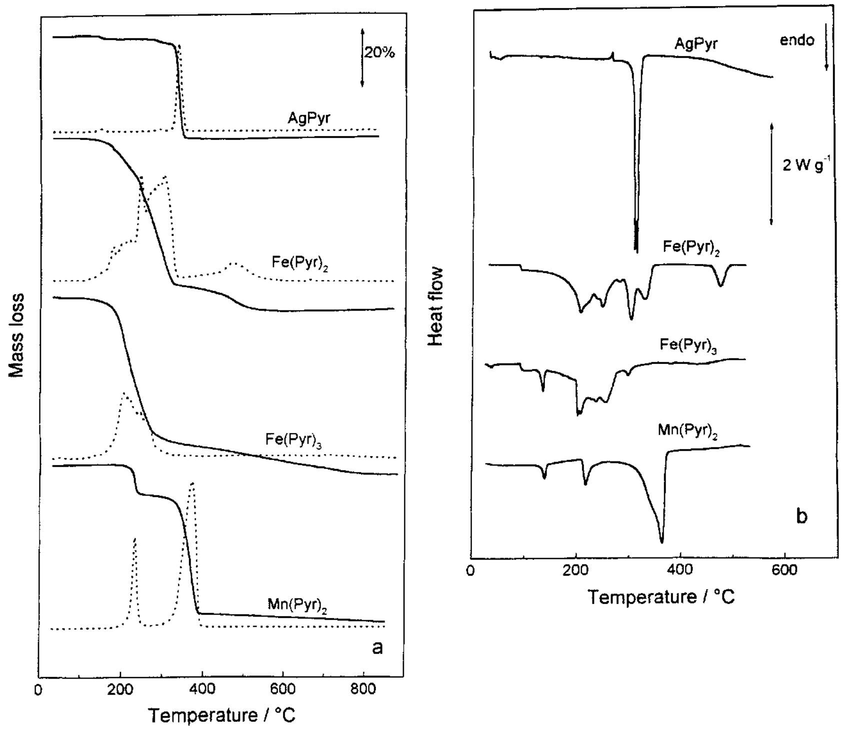

Fig. 2. (a) TG (solid)/DTG (dashed) and (b) DSC curves for the Pyr complexes under nitrogen flow of 90 ml min^{-1}, other conditions as in the text.

Table 3
TG (residues and temperature range) and DSC data corresponding to the decomposition of the Pip compounds

Process	Temperature interval (°C) (TG)	Residue (%)		DSC data[a], peak temperature (°C)
		TG	Calculated	
N_2 atmosphere				
AgPip → Ag_2S	199–350	48.5	42.1	233, 240 (exo)
$MnPip_2$ → MnS	178–390	27.8	23.2	247 (endo), 318 (endo)
MnS → $Mn_3O_4 + Mn_2O_3$	414–788	22.5	–	–
$FePip_2{\cdot}H_2O$ → Fe_2O_3	145–451	21.9	1.12	25–120 (endo)
$FePip_3{\cdot}H_2O$ → FeO + S	164–612	23.0	24.5	100, 200, 279 (endo)
Air atmosphere				
AgPip → $Ag_2SO_4 + AgO$	196–321	57.1	–	245 (exo), 295 (endo)
$Ag_2SO_4 + AgO$ → $Ag_2SO_4 + Ag$	538–599	49.2	–	430 (exo)
$Ag_2SO_4 + Ag$ → $Ag_2SO_4 + Ag$	600–>800	46.7	40.2	–
$MnPip_2$ → $MnSO_4 + Mn_3O_4 + Mn_2O_3$	90–516	23.1	–	130, 165, 210, 258, 415 (exo), 220 (endo)
$MnSO_4 + Mn_3O_4 + Mn_2O_3$ → $Mn_3O_4 + Mn_2O_3 + MnO_2$	722–842	19.9	20.3	–
$FePip_2{\cdot}H_2O$ → Fe_2O_3	122–239	21.7	20.5	256, 267 (exo)
$FePip_3{\cdot}H_2O$ → $Fe_2O_3 + Fe_2(SO_4)_3$	193–275	32.6	–	233, 269, 309 (exo)
$Fe_2O_3 + Fe_2(SO_4)_3$ → Fe_2O_3	350–>700	22.8	–	469 (exo)

[a] Exo: exothermic process; endo: endothermic process.

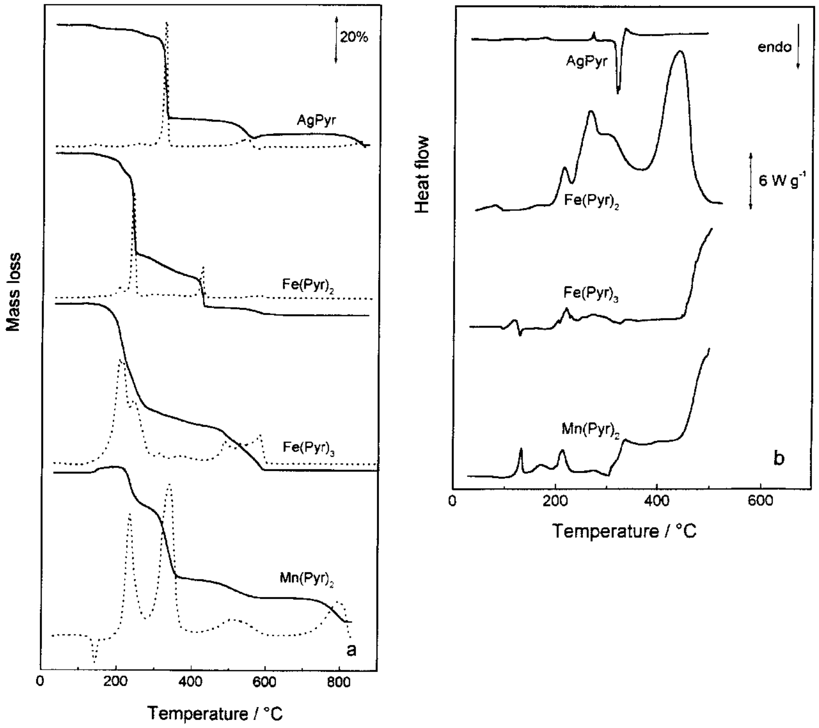

Fig. 3. (a) TG (solid)/DTG (dashed) and (b) DSC curves for the Pyr complexes under air flow of 90 ml min^{-1}, other conditions as in the text.

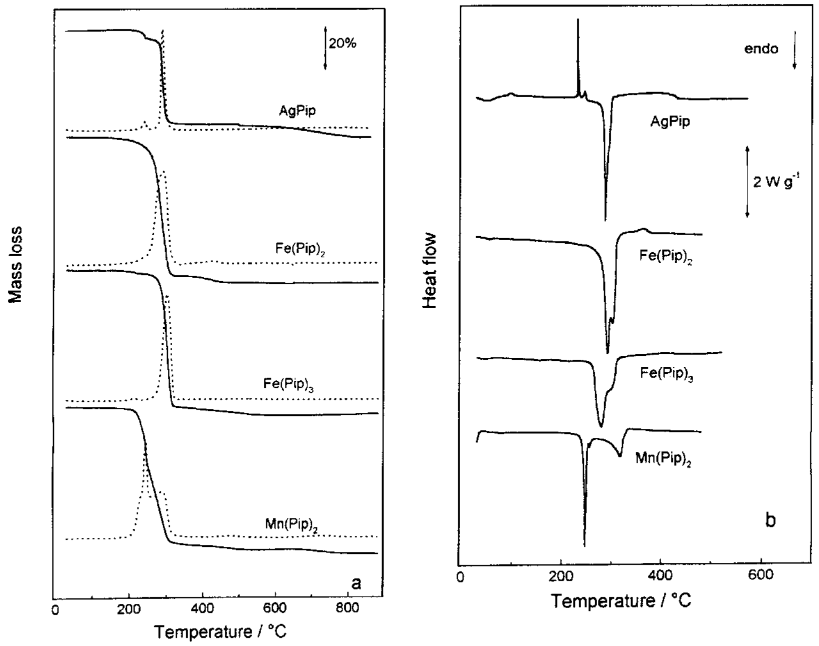

Fig. 4. (a) TG (solid)/DTG (dashed) and (b) DSC curves for the Pip complexes under nitrogen flow of 90 ml min^{-1}, other conditions as in the text.

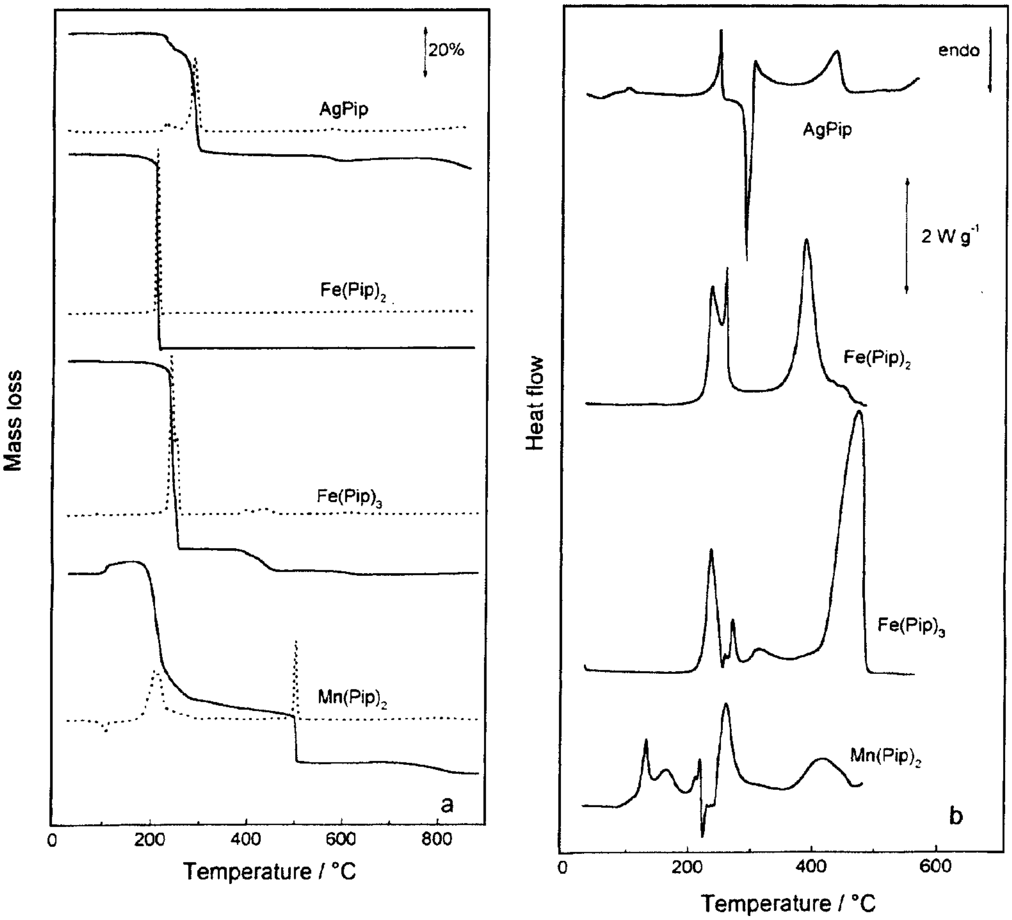

Fig. 5. (a) TG (solid)/DTG (dashed) and (b) DSC curves for the Pip complexes under air flow of 90 ml min^{-1}, other conditions as in the text.

The TG curves of all Pip complexes under nitrogen suggested a sudden one step decomposition process, with different profiles when compared to the Pyr analogues, except for AgPip complex which decomposed in a similar way as AgPyr. No evidence of reduction was observed for the Fe(III) complex, since TG/DTG and DSC curves are different from that for $FePip_2$. Under air the organic part of Fe(III) and Fe(II) complexes decomposed faster than in nitrogen. As in MnPyr, a mass gain was observed in TG curves of MnPip around 200°C.

The DSC curves of Pip complexes are completely different from the corresponding Pyr analogues in the respective atmospheres, except for the Ag complexes, in agreement with the differences observed in the IR spectra.

4. Conclusion

As evidenced by the thermoanalytical results the Pyr complexes (bidentate) presented much more complicated decomposition processes than the Pip analogues (monodentate). This should be related to the structural differences as indicated in the IR spectra. Silver complexes in which both ligands behave as monodentate presented similar decomposition profiles, as have been previously reported for other complexes of the same ligands [15,16]. A dehydration process is not clearly observed in the results obtained in the TG/DTG and DSC. This fact should be related to the iron affinity for the oxygen atom of water [21].

The influence of hydration water in the decomposition makes it impossible to define a thermal stability order for the complexes studied here.

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