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Article

The Effect of the Aminic Substituent on the Thermal Decomposition of Cyclic Dithiocarbamates

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Estudos termogravimétricos e calorimétricos diferenciais para ditiocarbamatos de NH_4^+, Na^+, Zn^{2+}, Cd^{2+} e Pb^{2+}, derivados de aminas cíclicas contendo nitrogênio como heteroátomos, foram realizados em atmosferas de ar e nitrogênio, para avaliar a influência da tensão angular dos anéis na decomposição térmica destes compostos, em relação à formação de tiocianatos metálicos como via de decomposição. Os intemediários formados foram caracterizados por difração de raios-X, tendo sido encontrados oxissulfatos de Zn^{2+}, Cd^{2+} e Pb^{2+}, sob atmosfera de ar, o que sugere a decomposição térmica nestas condições como via sintética para estes compostos. Os produtos de decomposição final obtidos foram sulfetos metálicos sob nitrogênio e óxidos dos metais de transição e sulfato de sódio sob ar. Entalpias de fusão são também descritas, com base nos resultados de DSC.

Thermogravimetric and Differential Scanning Calorimetric investigation of the thermal behaviour of NH_4^+, Na^+, Zn^{2+}, Cd^{2+} e Pb^{2+} dithiocarbamates obtained from cyclic amines, is described under nitrogen and air atmospheres in order to investigate the effect of a cyclic ring on the mechanism of decomposition. Intermediates were identified by X-ray Diffraction analysis. Zn^{2+}, Cd^{2+} e Pb^{2+} oxysulphates were detected under air atmosphere suggesting the thermal decomposition under these conditions as an alternating synthetic route to prepare those compounds. The final decomposition products were the metallic sulphides under N_2 atmosphere while transition metal oxides and sodium sulphate were obtained under air. Melting enthalpies are also reported from DSC data.

Keywords: *dithiocarbamates, thermogravimetry, differential scanning calorimetry, decomposition mechanism*

Introduction

Dithiocarbamates (DTC), are products of a reaction of a primary or secondary amines with carbon disulphide, and has been described in several applications such as medicine, industry, agriculture and chemistry, that are commented in several reviews[1-9].

In those reviews is possible to note that the knowledge of DTC thermal behaviour and information about their stability and decomposition residues, are important data and can show synthetic routes for unusual compounds.

In three reviews about the thermal behaviour of DTC compounds[1,2,4], most of references are related with the aliphatic derivatives in which a decomposition mechanism involving metallic thiocyanate as the main intermediate. However, few studies has been presented in relation to the cyclic DTC, such as pyrrolidinedithiocarbamate (Pyr) and piperidinedithiocarbamate (Pip), in which the formation of the thiocyanate must be related with cleavage of C-N bond in the ring.

Pyr complexes are widely used in solvent extraction and other analytical procedures, because of their resistance to acidic media[10]. In applications such as in atomic absorption spectrophotometry, the thermal decomposition data can help in understanding more about atomization mechanisms of those complexes[11].

The Pip complexes of Zn and Cd are largely applied as curing agents in rubber processing[12] and in photographic films[13,14] were the thermal behaviour is an important feature.

Recently Fernandez-Alba *et al.*[15], reported studies on thermal decomposition of NH_4Pyr and other DTC, with agricultural applications. Vibrational Spectroscopy was used to propose an structure to the complexes.

Diaz *et al.*[16] studied decomposition fragments in mass spectroscopy for Bi, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, Zn and ammonium in Pyr compounds.

Gomicek *et al.*[17], presented X-ray diffraction studies for the characterisation of decomposition products of several Pyr complexes with divalent cations. The decomposition products were obtained at 80, 150, 250, 300, 400 and 600 °C, under oxygen and argon atmospheres. The compounds were obtained in an oven without use of the TG to follow up the thermal decomposition pathways.

The same authors[18], investigated the thermal behaviour of Cd, Co, Cu, Fe, Ni, Pb and V - Pyr complexes in graphite tubes for atomic absorption.

Sceney *et al.*[19], studied the thermal decomposition of seven copper(II) dithiocarbamates by thermogravimetry, under air and nitrogen atmospheres. Complete TG and DTA studies are reported to copper(II)-diethyldithiocarbamate complex under air, vacuum and nitrogen.

It is also important to note that few DSC results, about thermal DTC behaviour has been previously reported. The most thermal differential data are from DTA results.

In the present work the thermal behaviour of ammonium, sodium, zinc, cadmium and lead complexes with Pyr and Pip under nitrogen and air atmospheres was investigated with the purpose of evaluating the influence of the different angular tension of the 5 and 6 members aminic rings on the decomposition and identify the intermediates formed.

Experimental

Syntesis of the ligands and complexes

Ammonium and sodium salts of the ligands, were prepared by direct reaction between the piperidine or pyrrolidine and carbon disulphide in basic media and recrystallised from acetone (NH_4Pip) or ethanol-water 1:1 (v/v) (NaPip, NaPyr and NH_4Pyr) and then dried in a vacuum oven at 50 °C, for 8 h.

The metallic complexes were obtained by direct reaction of the DTC sodium salt and a soluble salt of the desired cation. The resulting precipitates were filtered, washed with acetone and dried as above.

Equipment

Characterazation of the compounds was performed using Vibrational Spectroscopy (KBr pellets) in a Nicolet 5SXC spectrophotometer; NMR-^{1}H in a Brücker AC-200 spectrometer and Flame Atomic Absorption Spectroscopy in an Intralab AA12/1475 (Gemini) spectrophotometer and Elemental Analysis using a Fisons EA 1108 CNHS-O instrument.

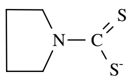
TG curves were recorded in a DuPont 9900 thermoanalyser coupled with a TGA 951 Thermogravimetric Module under a gas flow of 200 mL min^{-1} (N_2 or air), in a platinum crucible, at 10 °C min^{-1} heating rate and using samples of about 7 mg of each compound at atmospheric pressure. For the ammonium salts (Pyr and Pip), the TG experiments were carried out only in nitrogen. The DSC curves were recorded in a DuPont 9900 thermoanalyser coupled with a DSC 910 Calorimetric Module under a gas flow of 200 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.

X-ray diffraction patterns of intermediates and final products, were obtained in an HZ-Karl Zeiss or a D5.000 Siemens diffractometers. The melting points were also determined in a dry furnace Electrothermal digital melting point apparatus.

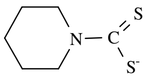
Fusion enthalpies were determined by DSC after calibration of the equipment with indium metal. The area of the melting peak for this metal was stored in the system and compared with the area of sample melting peaks in a standard procedure. Temperatures are also measured in relation to the In fusion, calibration.

Results and Discussion

The structural formula of the ligands are:

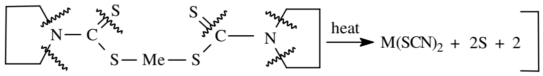


Pyr



Pip

The proposition of the earlier works for thiocyanate[1] as the decomposition intermediate implies that the decomposition of the DTC complexes occurs with rupture of C-N-C bonds. For a divalent cation-Pyr complex we can propose:



(1)

The differences in the angular tension between the 5 and 6 membered rings of pyrrolidine and piperidine respec-

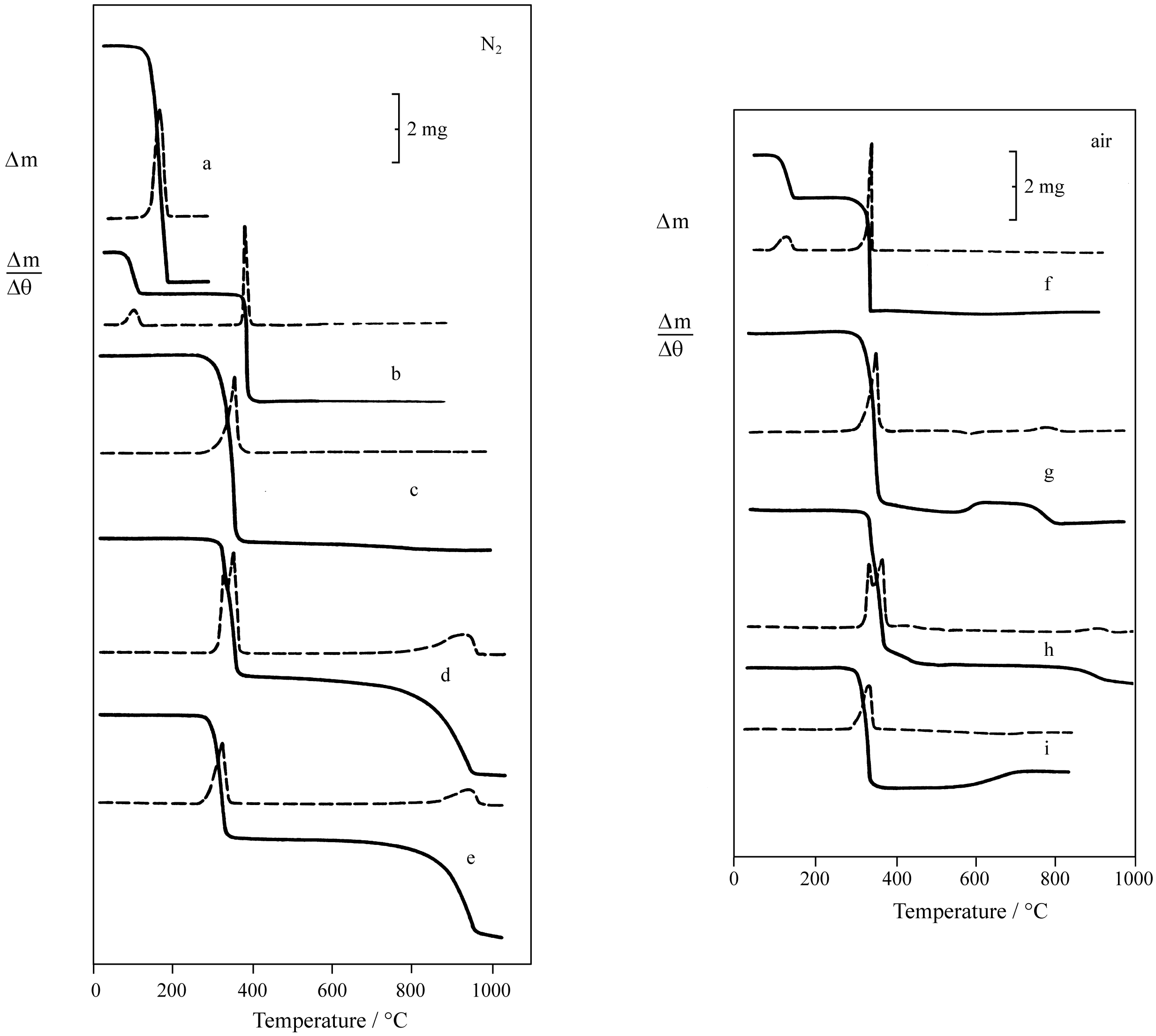


Figure 1. TG (solid line) and DTG (dashed line) curves for the Pyrrolidinedithiocarbamates under N_2 atmosphere: a) NH_4^+; b) Na^+; c) Zn^{2+}; d) Cd^{2+}; e) Pb^{2+}; and under air: f) Na^+; g) Zn^{2+}; h) Cd^{2+} and i) Pb^{2+}.

tively suggests that Pyr derivatives, a more tense 5 member ring, are supposed to decompose preferentially by the thiocyanate.

However the results obtained here suggest the decomposition in a direct way (except to $CdPyr_2$), without the thiocyanates as the main decomposition pathway, in agreement with some observations of Fernandez-Alba *et al.*[15]

The spectrometric characterisation results are shown in Table 1 and the elemental analysis data for all the compounds are shown is in Table 2. The TG-DTG curves for Pyrrolidinedithicarbamates are shown in Fig. 1 under nitrogen and air atmospheres. The DSC curves under both atmospheres are in Fig. 2.

Mass losses, temperature ranges and residues for the decomposition of all Pyr compounds are described in Table 3. The melting points and enthalpies are shown in Table 4.

NH_4Pyr

The TG/DTG curves of ammonium salt showed a single decomposition step between 70 and 175 °C (Fig 1.a) without residues on the crucible. The DSC curves of ammonium salt showed endothermic peaks at 139, 164, 191 and 199 °C under nitrogen atmosphere (Fig. 2.a). Under air (Fig. 2.f) the peaks are at 141, 163, 186 and 195 °C.

In order to attribute the peaks a sample was heated in a glass tube (20 x 2 cm) immerse in a glycerine bath. Around 140 °C the gas produced by heating the sample was bubbled into a phenolphtalein solution turning it to red and showed a characteristic smell of ammonia[26]. Near 150 °C melting of sample was observed producing a brown viscous liquid, which IR spectra suggests that it is the HPyr (Table 1). The gas at 165 °C when bubbled in a Sb^{3+} solution produced an orange solid and showed a characteristic smell of H_2S. The colour is characteristic for Sb_2S_3 [26].

According to these observations it was shown that the NH_4Pyr decomposes by the following steps:

$$NH_4Pyr \rightarrow NH_3 + Hpyr \qquad (2)$$

$$HPyr_{(s)} \rightarrow HPyr_{(l)} \qquad (3)$$

Table 1. Molecular absorption spectrometry (UV), infrared spectrometry (IR) and nuclear magnetic resonance ^1H (NMR) data obtained for the compounds.

Compound	UV	IR bands / cm^{-1}			NMR
	λ_{MAX}/nm (log)	ν(C=S)	ν(N-CS_2)	ν(C-N)	ν / ppm
HPyr		996	1160	1455	
NH_4Pyr	264(4.0)-280(4.0)^a	996	1159	1392	1.9; 3.4; 3.8
NaPyr	264(4.0)-280(4.0)^a	$998^{(1005c)}$	$1160^{(1129c)}$	$1421^{(1420c)}$	1.8; 3.5
$ZnPyr_2$		1003	1161	$1482^{(1485d)}$	2.0; 3.7
Cd Pyr_2		994	1160	$1471^{(1475e)}$	f
Pb Pyr_2		1000	1162	$1509^{(1460e)}$	2.0; 3.8
NH_4Pip	256(4.1)-278(4.0)^a	993	1117	1400	1.6; 1.8; 3.2; 3.6
NaPip	256(4.1)-278(4.0)^a	$1005^{(1003c)}$	$1110^{(1110c)}$	$1470^{(1465b)}$	1.4; 2.0; 4.0
$ZnPip_2$		979	1113	1484	1.5; 1.7; 4.0
Cd Pip_2		975	1112	1482	1.5; 1.7; 4.1
Pb Pip_2		973	1002	1464	1.5; 1.7; 3.9

a. in agreement with Ref. 20, 21; b. Ref. 22; c. Ref. 23; d. Ref. 24; e. Ref. 25; f. insoluble in deutered water.

Table 2. Analytical data of the compounds (%).

Compound		Metal	C	H	N
NH_4Pyr	calc.	-	36.55	7.38	17.05
	found	-	36.59	7.61	17.11
$NaPyr.2H_2O$	calc.	11.20	29.25	5.90	6.82
	found	10.90	29.31	5.83	6.87
$ZnPyr_2$	calc.	18.26	33.55	4.51	7.89
	found	18.79	33.57	4.62	7.81
Cd Pyr_2	calc.	27.76	29.66	3.99	6.92
	found	27.20	29.69	3.90	6.88
Pb Pyr_2	calc.	41.46	24.03	3.23	5.61
	found	40.50	24.15	3.30	5.66
NH_4Pip	calc.	-	40.41	7.93	15.71
	found	-	39.98	7.84	15.79
$NaPip.2H_2O$	calc.	10.48	32.85	6.45	6.39
	found	10.79	32.92	6.51	6.25
$ZnPip_2$	calc.	16.94	37.34	5.23	7.26
	found	17.46	37.41	5.19	7.21
Cd Pip_2	calc.	25.96	33.29	4.66	6.47
	found	25.80	33.21	4.60	6.52
Pb Pip_2	calc.	39.26	27.31	3.83	5.31
	found	40.69	27.40	3.74	5.28

Table 3. Mass loses and temperature range corresponding to the decomposition of the pyr compounds.

Thermal Process	Temp. Interval / °C	Mass Loss or residue/ %	
		TG	Calc.
N_2 Atmosphere			
$NaPyr.2H_2O \rightarrow NaPyr + 2H_2O$	61-131	17.6[a]	17.5
$NaPyr \rightarrow Na_2S_{3.3}$	340-394	36.5[b]	37.0
$ZnPyr_2 \rightarrow ZnS$ (+ Zn)	243-389	22.0[b]	25.9
$ZnS \rightarrow Zn$	389-811	18.5[b]	18.3
$CdPyr_2 \rightarrow CdS$ (+ C)	280-421	42.5[b]	35.7
$CdS_{(S)} \rightarrow CdS_{(g)}$	566-961	0[b]	3.52
$PbPyr_2 \rightarrow PbS$	272-390	49.5[b]	48.0
$PbS_{(s)} \rightarrow PbS_{(g)}$	673-1030	0[b]	9.02
Air Atmosphere			
$NaPyr.2H_2O \rightarrow NaPyr + 2H_2O$	71.7-130	17.5[a]	17.5
$NaPyr \rightarrow Na_2SO_4$	217-324	35.2[b]	34.6
$ZnPyr_2 \rightarrow ZnS$	250-479	26.7 [b]	27.2
$ZnS \rightarrow ZnSO_3 + ZnS$	540-594	30.4 [b]	-
$ZnSO_3 + ZnS \rightarrow ZnO$	711-788	21.7 [b]	22.7
$CdPyr_2 \rightarrow CdS$	277-470	33.9 [b]	35.7
$CdS \rightarrow Cd_3OSO_4$	564-670	37.5 [b]	37.0
$Cd_3OSO_4 \rightarrow CdO$	779-942	31.4 [b]	31.7
$PbPyr_2 \rightarrow PbS + PbSO_4$	272-367	51.2 [b]	-
$PbS \rightarrow PbSO_4$	367-711	59.0 [b]	60.7

- not calculated, mixture; a: relative to a mass loss; b: relative to the residue.

Table 4. Melting points and energies, determined by dsc and capillary tubes.

Compound	Atmosphere	DSC		Capillary / °C
		Temperature / °C	$\Delta_{fus}H_m$ / J mol^{-1}	
NH_4Pyr	N_2/air	163.8	*	150
$ZnPyr_2$	N_2	293.8	25.3	294
	air	293.6	25.3	
$PbPyr_2$	N_2	286.0	37.5	286
	air	285.1	34.2	
NaPip	N_2	301.7	19.7	296
	air	**	**	
$ZnPip_2$	N_2	228.4	36.9	228
	air	228.2	35.4	
$CdPip_2$	N_2	258.2	30.3	259
	air	258.3	30.1	
$PbPip_2$	N_2	244.6	37.5	244
	air	258.1	35.9	

* base line not clear for integration procedure; ** masked by the decomposition process.

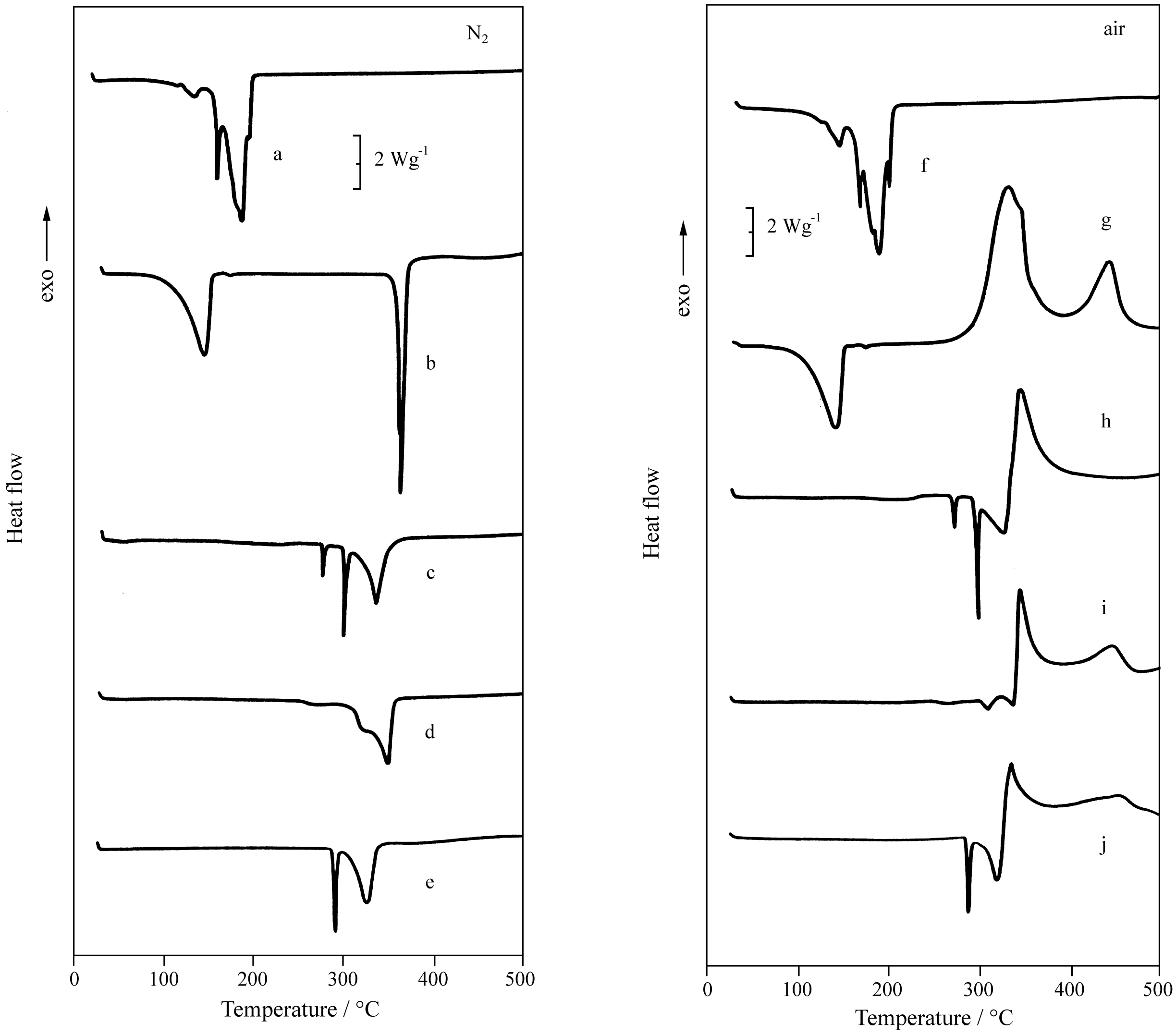


Figure 2. DSC curves for the Pyrrolidinedithiocarbamates under N_2 atmosphere: a) NH_4^+; b) Na^+; c) Zn^{2+}; d) Cd^{2+}; e) Pb^{2+}; and under air: f) NH_4^+ g) Na^+; h) Zn^{2+}; i) Cd^{2+} and j) Pb^{2+}.

$$HPyr_{(l)} \rightarrow H_2S + \text{other volatiles} \qquad (4)$$

As the DSC experiments were carried out in an hermetic crucible the temperatures are higher than the observed in the open tube. These observations are not described in the earlier reports. When the DSC experiment is carried out in an open crucible, a single peak at 155 °C is observed, under both atmospheres. In the TG experiments these features are not observed probably because the crucible is open.

NaPyr

Sodium salt showed the decomposition in two steps, relative to the loss of $2H_2O$, with sodium polissulphide and a carbonaceous residue under nitrogen atmosphere (340-394 °C) according to Figure 1.b and sodium sulphate air (Fig. 1.f), and it was the most stable compound in the series here studied. The presence of the polisuphide is in agreement with the observed in earlier works[27,28], and were characterised by X-ray diffraction.

The DSC curves for sodium salt evidenced peaks attributed to a loss of water and decomposition under N_2 (Fig. 2.b). The experiment carried out in air (Fig. 2.g) showed the loss of water followed by exothermic processes of decomposition and oxidation to Na_2SO_4, respectively.

ZnPyr$_2$

TG/DTG curves of zinc compound showed decomposition in a single step resulting mainly in ZnS and a small amount of Zn ° in the residue under nitrogen (Fig. 1.c). This mixture is slowly reduced up to 811 °C producing Zn°. Under air (Fig. 1.g) three steps were observed. The first was the decomposition and formation of ZnS, followed by production of $ZnSO_3$ and ZnS and pure ZnO. All these data were confirmed by X-ray diffraction data.

The DSC curves under N_2 atmosphere (Fig. 2.c), showed a endothermic peak at 269 °C ($\Delta H = 8.32$ kJ mol^{-1}), attributed to a crystalline phase change followed by a melting process, coincident with the observation in a capillary tube. The endothermic peak at 331 °C, was attributed to decomposition of the compound. Under air atmosphere (Fig. 2.h) endothermic peaks at 268 °C ($\Delta H = 8.40$ kJ mol^{-1}), and at 294 °C, were attributed to crystalline phase change and melting respectively, in agreement with the data under nitrogen atmosphere. The decomposition of the complex is represented by endothermic peaks at 325 and exothermic at 346 °C. $ZnPyr_2$, is the unique compound that showed crystalline phase transition in the present series.

$CdPyr_2$

The TG curves in N_2 atmosphere (Fig. 1.d) showed the decomposition with generation of CdS and a amorphous material according the X-ray diffraction data. The black amorphous material was insoluble in HCl and was suspect to carbonaceous residue.

The DTG curve suggests that the first step is split in two consecutive reactions. This could be related with the formation of thiocyanide considering that the Cd^{2+} is soft acid with affinity to soft base represented by that anion, according to Pearson's concept[29] and the weakening of the C-N ring bonds by angular tension. Above 566 °C volatilisation of the CdS is observed, represented by a yellow substance impregnating the exhausting furnace tube, with black residue of 3.6% at the crucible, probably carbon.

Under air atmosphere (Fig. 1.h) the residues showed the presence of CdS at 400 °C and pure Cd_3OSO_4 at 700 °C. The final residue is CdO. All these results were confirmed by X-ray diffraction data.

The DSC curves do not evidenced the occurrence of melting in agreement with capillary tube observation. Under N_2 atmosphere (Fig. 2.d), is possible to note the decomposition, related with the endothermic peaks at 320 and 345 °C. Under air atmosphere (Fig. 2.i) decomposition is represented by the peaks at 309, 336 °C and 346 °C in agreement with TG data. The exothermic processes at 446 °C, was attributed to carbon burning.

$PbPyr_2$

Under nitrogen atmosphere (Fig. 1.e) the $PbPyr_2$ TG curves showed two steps. The first one resulting in a black residue of PbS, confirmed by X-ray diffraction measurements and by smell of H_2S in presence of hydrochloric acid. The second step was related to volatilization of the PbS; resulting in a small amount of intermetallic Pb-Pt at crucible, at 1030 °C, according the X-ray diffraction data.

Under air atmosphere (Fig. 1.i) the decomposition occurred with formation of a mixture of PbS and $PbSO_4$, followed by oxidation to $PbSO_4$ and a small amount lead oxysulphate, $Pb_3O_2SO_4$, according the X-ray diffraction results.

The DSC curve under N_2 atmosphere (Fig. 2.e), showed a sharp endothermic peak, attributed to the melting, followed by an endothermic decomposition peak at 321 °C. The curve in air (Fig. 2.j) also suggests a melting process. In the sequence occurred the decomposition of compound with peaks at 320 °C and at 334 °C, followed by the oxidation process represented by the exothermic peak at 453 °C.

The TG-DTG curves for Piperidinedithicarbamates are shown in Fig. 3 under nitrogen and air atmospheres. The DSC curves under both atmospheres are in Fig. 4. Mass losses, temperature ranges and residues for the decomposition of all Pyr compounds are described in Table 5. The melting points and enthalpies are shown in Table 4.

NH_4Pip

The TG/DTG curves of this salt showed a single mass loss (85-180 °C), without residues in the crucible (Fig. 3.a). The DSC curves showed a sharp endothermic peak, at 172 °C and 175 °C under N_2 (Fig. 2.a) and air (Fig. 2.f) atmospheres respectively, without evidence of melting. Experiment in an open glass tube showed that the compound sublimates without decomposition since the IR spectra of the sublimate product is identical to the original salt.

NaPip

This salt showed a very similar behaviour with the NaPyr. The decomposition occurred in two steps under N_2 (Fig. 3.b). The first relative to the loss of $2H_2O$, in agreement with Kudela *et al.* report[23]. The second step is related to decomposition and formation of sodium polisulphide as residue under nitrogen[27,28]. Under air (Fig. 3.f) the TG curve showed the water loss was and formation of sodium sulphate in the range. All these residues were confirmed by X-ray diffraction, being the most stable piperidine derivative in the series here studied.

The DSC curves for sodium salt showed three endothermic peaks under N_2 atmosphere (Fig. 4.b). The first at 142 °C related to the water loss, the second a sharp peak at 302 °C, attributed to a melting process. The last one at 338 °C, was attributed to the decomposition. Under air (Fig. 4.g) showed the loss of water (endothermic peaks at 148 and 165 °C), followed by complex exothermic processes of decomposition represented by the peaks at 291 and 320 °C and oxidation to Na_2SO_4 at 417 °C. The melting is probably masked by the strong exothermic decomposition of the compound under oxidative atmosphere.

Table 5. Mass loses and temperature range corresponding to the decomposition of the pip compounds.

Thermal Process	Temp. Interval / °C	Mass Loss or residue/ %	
		TG	Calc.
N_2 Atmosphere			
$NaPip.2H_2O \rightarrow NaPip + 2H_2O$	64-126	16.3[a]	16.4
$NaPip \rightarrow Na_2S_2$	297-362	25.2 [b]	25.1
$ZnPip_2 \rightarrow ZnS$ (+ Zn)	228-400	24.6 [b]	25.2
$ZnS \rightarrow Zn$	541-951	16.8 [b]	17.0
$CdPip_2 \rightarrow CdS + C$	240-423	37.2 [b]	33.4
$CdS_{(S)} \rightarrow CdS_{(g)}$	660-954	3.90 [b]	0
$PbPip_2 \rightarrow PbS$	232-394	46.0 [b]	45.3
$PbS_{(s)} \rightarrow PbS_{(g)}$	702-1030	3.47 [b]	0
Air Atmosphere			
$NaPip.2H_2O \rightarrow NaPip + 2H_2O$	66-130	16.1[a]	16.4
$NaPip \rightarrow Na_2SO_4$	233-324	32.0 [b]	32.4
$ZnPip_2 \rightarrow ZnS + ZnSO_3$	226-379	25.0 [b]	-
$ZnS + ZnSO_3 \rightarrow ZnO + ZnSO_4$	379-444	23.1 [b]	-
$ZnSO_4 \rightarrow ZnO$	690-748	20.3 [b]	21.0
$CdPip_2 \rightarrow CdS + C$	241-360	37.5 [b]	33.4
$CdS \rightarrow Cd_3OSO_4$	482-739	35.7 [b]	34.5
$Cd_3OSO_4 \rightarrow CdO$	799-916	30.1 [b]	29.7
$PbPip_2 \rightarrow PbS$ (+ Pb_2OSO_4)	253-389	49.5 [b]	45.3
$PbS \rightarrow Pb_2OSO_4$	389-508	52.0 [b]	50.2
$Pb_2OSO_4 \rightarrow PbSO_4$	549-730	57.9 [b]	57.5

- not calculated, mixture; a: relative to a mass loss; b: relative to the residue.

ZnPip₂

TG/DTG curves of zinc compound showed decomposition in a single step under nitrogen atmosphere (Fig. 3.c) resulting in a white residue confirmed by HCl test and X-ray diffraction as the. This is slowly reduced to Zn°. Under air atmosphere (Fig. 3.g) there was three steps of decomposition, resulting in a mixture of ZnS and $ZnSO_3$ at 379 °C; ZnO and $ZnSO_4$ at 444 °C and ZnO at 748 °C. All these compounds were identified by their X-ray diffraction patterns.

The DSC curves under N_2 atmosphere (Fig. 4.c), showed a endothermic peaks at 228 and 332 °C, attributed to melting and decomposition of the compound respectively. Under air atmosphere (Fig. 4.h) endothermic peak at 228 °C is observed related to the melting, in agreement with nitrogen experiments. The decomposition of the complex is represented by the peaks at 329 and at 347 °C.

The melting point is in disagreement with that of Oktavec *et al.*[30], who describes that it occurs at 288-289 °C.

CdPip₂

The TG/DTG curves showed that the decomposition occurred in two steps under N_2 atmosphere (Fig. 3.d) generating CdS which is present as a yellow residue, confirmed by X-ray diffraction and HCl test. The difference between the TG and calculated residues is due to the presence of carbonaceous residue, represented by amorphous phase in X-ray diffraction. Finally volatilization of CdS is observed, with a black residue of 3.9% exactly the difference at 423 °C, attributed to the carbonaceous material.

Under air atmosphere (Fig. 3.h) the main decomposition step occurred producing CdS and carbonaceous material followed by oxidation lead to the Cd_3OSO_4 and finally CdO as the final product of decomposition. All these products were characterised by X-ray diffraction patterns.

The DSC curves evidenced the occurrence of melting represented by the peaks at 258 °C under N_2 (Fig. 4.d) and at 258 °C under air atmosphere (Fig. 4i). Decomposition were represented by the endothermic peak at 323 under N_2.

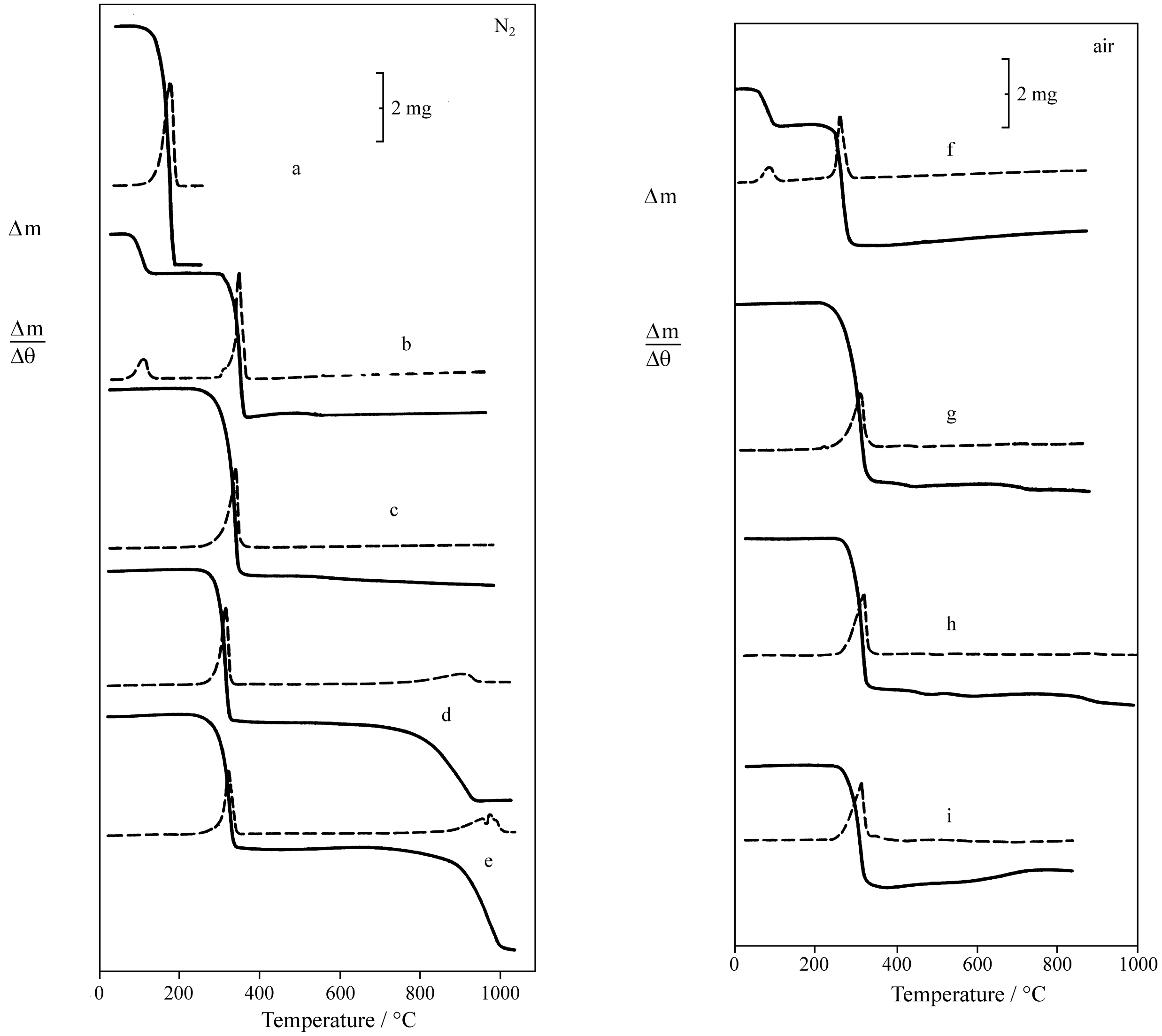


Figure 3. TG (solid line) and DTG (dashed line) curves for the Piperidinedithiocarbamates under N_2 atmosphere : a) NH_4^+; b) Na^+; c) Zn^{2+}; d) Cd^{2+}; e) Pb^{2+}; and under air: f) Na^+; g) Zn^{2+}; h) Cd^{2+} and i) Pb^{2+}.

Under air the peaks at 321 and 335 °C were attributed to the decomposition, and the exothermic peak at 448 °C was related with the production of Cd_3OSO_4.

PbPip$_2$

The TG/DTG curves under nitrogen (Fig. 3.e) for the lead compound showed a decomposition, resulting in a black residue of PbS confirmed by X-ray diffraction and test with HCl. Above 700 °C, volatilization of the PbS occurred, similarly to the $PbPyr_2$.

Under air atmosphere (Fig. 3.i) a decomposition occurred, with formation of a mixture of PbS and traces of lead oxysulphate Pb_2OSO_4. Then the mixture is converted to Pb_2OSO_4, and finally $PbSO_4$. The residues were identified by X-ray diffraction.

The DSC curve under N_2 atmosphere (Fig. 4.e), showed a sharp endothermic peak at 244 °C attributed to melting, followed by a decomposition peak at 323 °C. The curve under air atmosphere (Fig. 4.j) showed the melting peak. At the sequence the decomposition of the compound is observed with peaks at 316 °C, 333 °C, and 416 °C.

Final Comments

It was expected that the angular tension in the five-membered pyrrolidine ring, should lead to a weakening of the C-N ring bonds favouring its rupture generating the metallic thiocyanate but this is not true.

According to the results obtained here, both cyclic DTC, decomposed preferentially in a direct way, without the formation of a thiocyanate intermediate, in a different

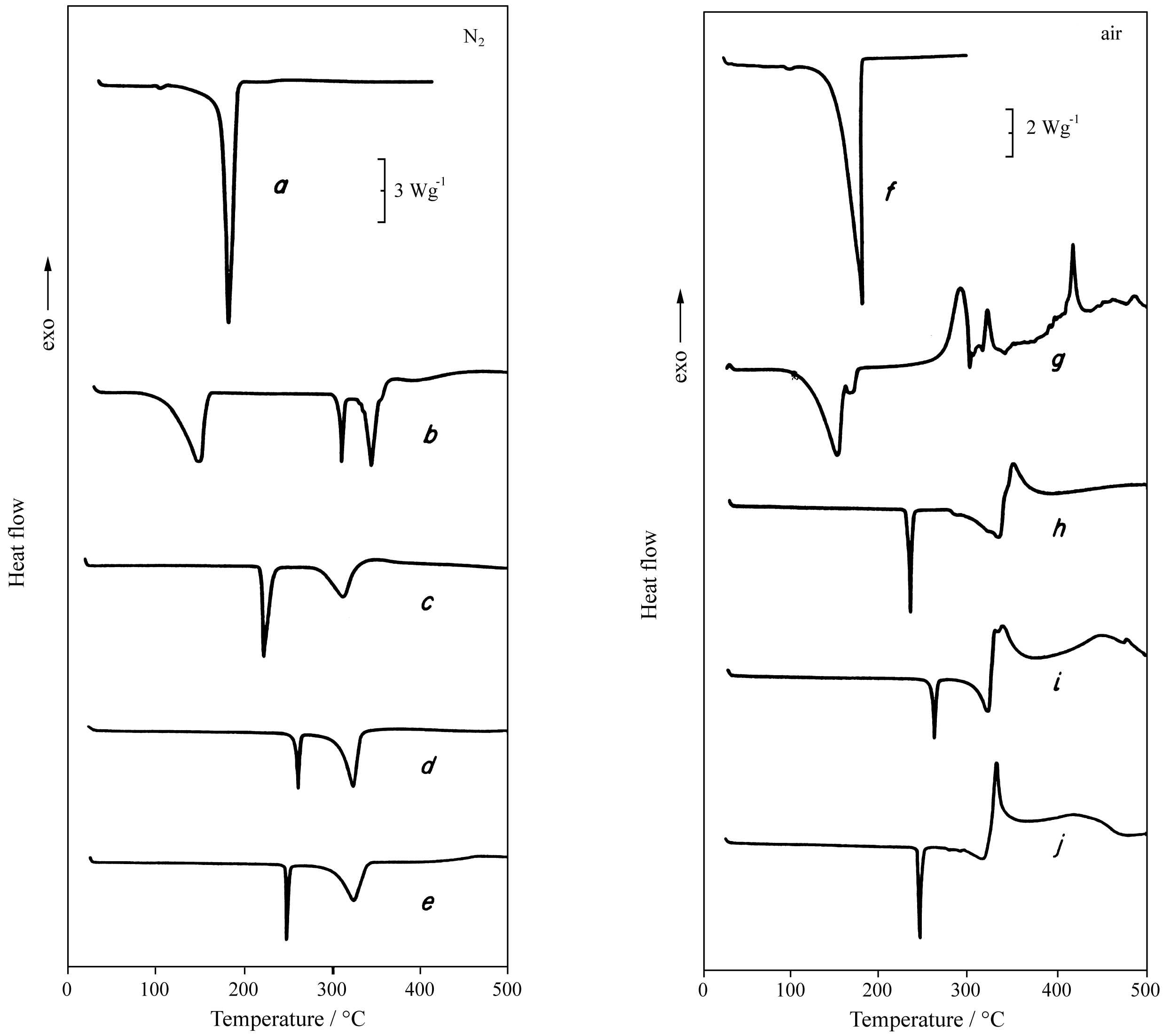


Figure 4. DSC curves for the Piperidinedithiocarbamates under N_2 atmosphere: a) NH_4^+; b) Na^+; c) Zn^{2+}; d) Cd^{2+}; e) Pb^{2+}; and under air: f) NH_4^+ g) Na^+; h) Zn^{2+}; i) Cd^{2+} and j) Pb^{2+}.

behaviour described to non cyclic derivatives[1]. The CdPyr suggested the unique exception.

The most remarkable difference in the decomposition as a function of the aminic group was observed for the ammonium salts.

Some oxysulphates were obtained as products, suggesting that the thermal decomposition of the dithiocarbamate complexes may be an useful synthetic route to obtain such compounds.

References

1. Sharma, A.K. *Thermochim. Acta* **1986**, *104*, 339.
2. Magee, R.J.; Hill, J.O. *Rev. Anal. Chem.* **1985**, *8*, 5.
3. Bond, A.M.; Martin, R.L. *Coord. Chem. Rev.* **1984**, *54*, 23.
4. Sengupta, S.K.; Kumar, S. *Termoch. Acta* **1984**, *72*, 349.
5. Hill, J.O.; Magee, R.J. *Rev. Inorg. Chem.* **1981**, *3*, 141.
6. Coucovanis, D. *Progr. Inorg. Chem.* **1979**, *26*, 301.
7. Coucovanis, D. *Progr. Inorg. Chem.* **1970**, 11, 233.
8. Hulanicki, A. *Talanta* **1967**, *14*, 1371.
9. Thorn, G.D.; Ludwig, R.A. *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam, 1962.
10. Vandebeek, R.R.; Joris, S.J.; Aspila, K.I.; Chakrabarti, C.L.*Can. J. Chem.* **1970**, *48*, 2204.
11. Santos, D.M.; Lucas, P.O.; Cavalheiro, E.T.G.; Nóbrega, J.A. 5th Rio Symposium on Atomic Spectrometry, Cancun, Mexico, 1998.
12. Datta, R.N.; Das, P.K.; Basu, D.K. *Rubber Chem. Technol.* **1984**, *57*, 879.

13. Fukumoto, H.; Tanaka, K.; Kawagishi, Y. *Jpn. Kokai Tokkio Koho,* J.P. 61.246.760, 1986.
14. Fukumoto, H.; Tanaka, K.; Kawagishi, Y. *Jpn. Kokai Tokkio Koho,* J.P. 61.246.757, 1986.
15. Fernandez-Alba, A.; Perez-Alvarez, I.J.; Martinez-Vidal, J.L.; Gonzalez-Pradas, E. *J. Thermal Anal.* **1992**, *211*, 271.
16. Diaz, J.R.; Zigon, M.; Gomicek, S. *Org. Mass Spectrom.* **1981**, *16*, 12.
17. Gomicek, S.; Golic, L.; Lengar, Z. *Anal. Chim. Acta* **1975**, *79*, 296.
18. Gomicek, S.; Lengar, Z.; Cernetic, J.; Hudnik, V. *Anal. Chim. Acta* **1974**, *73*, 97.
19. Sceney, C.G.; Hill, J.O.; Magee, R.J. *Termochim. Acta* **1975**, *11*, 301.
20. Lee, A.W.M.; Chan, W.H.; Chiu, C.M.L.; Tang, K.T. *Anal. Chim. Acta* **1989**, *218*, 157.
21. Oktavec, D.; tefanec, J.; Síle, B.; Konecny, V.; Garaj, J. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2487.
22. Desseyn, H.O.; Fabretti, A.C.; Forghieri, F.; Preti, C. *Spectrochim. Acta* **1985**, *41A*, 1105.
23. Kudela, S.; Garaj, J.; Hofbauerova, H.; Kettmann, V. *Collect. Czech. Chem. Commun.* **1980**, *45*, 800.
24. Kellner, R. *Mikrochim. Acta* **1975**, *II*, 24.
25. Kellner, R.; Prokopowski, P.; Malissa, H. *Anal. Chim. Acta* **1974**, *68*, 401.
26. Vogel, A.I. *Química analítica Qualitativa*; Trad. A. Gimeno; Mestre Jou, São Paulo, 1979.
27. Forghieri, F.; Preti, C.; Tassi, L.; Tosi, G. *Polyhedron* **1988**, *7*, 1231.
28. Fabretti, A.C.; Forghieri, F.; Giusti, A.; Preti, C.; Tosi, G.*Spectrochimica Acta* **1984**, *40A*, 343.
29. Huhey, J.E.; Keiter, E.A.; Keiter, R.L. *Inorganic Chemistry*, 4th Edition, Harper Collins, New York, 344-348, 1993.
30. Oktavec, D.; tefanec, J.; Síle, B.; Konecny, V.; Beinrohr, E.; Garaj, J. *Collect. Czech. Chem. Commun.* **1982**, *47*, 2867.

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