

Solution and Solid State Thermal Stability of Morpholinedithiocarbamates

Patrícia A. Antunes^a, Susete T. Breviglieri^a, Gilberto O. Chierice^a and Éder T. G. Cavalheiro^{b*}

^aInstituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970, São Carlos - SP, Brazil

^bDepartamento de Química, Universidade Federal de São Carlos, CP 676, 13565-905, São Carlos - SP, Brazil

Estudos termogravimétricos e calorimétricos diferenciais de morfolinoditiocarbamatos de NH_4^+ , Mn^{2+} , Co^{2+} , Ni^{2+} e Cu^{2+} foram realizados em atmosferas de ar e nitrogênio, para avaliar a influência da presença do oxigênio como heteroátomo no anel da amina na decomposição térmica. Produtos de decomposição térmica foram caracterizados através de difratogramas de raios X, sendo predominantemente formados por sulfetos metálicos, sob atmosfera dinâmica de nitrogênio e óxidos metálicos, sob ar. Usando espectrofotometria, também foram determinados o $\text{pK}_a = 3,56$ para o ácido morfolinoditiocarbâmico em força iônica $0,50 \text{ mol dm}^{-3}$ (NaClO_4) à $25,0 \text{ }^\circ\text{C}$ e parâmetros cinéticos de decomposição em diferentes valores de pH ($k_{\text{lim}} = 0,14 \pm 0,04 \text{ s}^{-1}$ e $t_{1/2 \text{ lim}} = 5,3 \pm 1,2 \text{ s}$).

Thermogravimetric and differential scanning calorimetric investigation of the thermal behavior of NH_4^+ , Mn^{2+} , Co^{2+} , Ni^{2+} e Cu^{2+} morpholinedithiocarbamates were performed under nitrogen and air atmospheres in order to investigate the effect, in the thermal decomposition, of the presence of an oxygen as the heteroatom in the amine ring. Decomposition products were identified by their X-ray diffraction patterns. Metal sulfites and oxides were the major residues under nitrogen and air atmospheres, respectively. Spectrophotometric measurements were used to estimate the $\text{pK}_a = 3.56$ for the morpholinedithiocarbamic acid at 0.50 mol dm^{-3} ionic strength (NaClO_4) at $25.0 \text{ }^\circ\text{C}$ and kinetic parameters of decomposition at different pH values ($k_{\text{lim}} = 0.14 \pm 0.04 \text{ s}^{-1}$ e $t_{1/2 \text{ lim}} = 5.3 \pm 1.2 \text{ s}$).

Keywords: morpholinedithiocarbamates, thermogravimetry, differential scanning calorimetry, decomposition rate constant

Introduction

Recently, the interest in the stability of dithiocarbamates (DTC) has been renewed by the utilization of such compounds as coadjuvants in the treatment of AIDS^{1,2}. They have also been suggested for tuberculosis³ and cancer⁴ treatment in the past. In these applications the compound must have enough chemical stability for an effective action in the biological medium. The DTC are obtained by the reaction between a primary or secondary amine with carbon disulfide in a basic aqueous solution. The applications of this class of compounds in medicine, agriculture, industry, analytical and organic chemistry, as well as their physicochemical properties are summarized in several review articles⁵⁻¹⁴. From these works and references cited therein it is known that DTC derived from cyclic amines are more stable than the aliphatic derivatives. Additionally the thermal behavior is another important feature in industry and agriculture applications.

The stability of DTC in solution is pH dependent and was investigated by different authors¹⁵⁻²¹. Chakrabarti and co-workers¹⁸⁻²¹ proposed a decomposition intermediate in which the water plays an important role.

Since the decomposition of the DTC's is very fast in acidic media a spectrophotometric method based on diode-array measurements has recently been proposed²², for a more accurate determination of the pK_a of dithiocarbamic acids. A correlation between the infrared spectroscopy data of the coordination nature of cyclic DTC complexes and its effect in thermal decomposition of such compounds has also been presented^{23,24}.

In this work, the pK_a value of the morpholinedithiocarbamic acid (HMor) was determined ($I = 0,50 \text{ mol dm}^{-3}$), by absorption spectrophotometry in the ultra-violet region, and used to estimate the rate of decomposition of morpholinedithiocarbamate (Mor) in different pH values. The thermal behavior of solid state complexes of the type $[\text{MMor}_2] \cdot x\text{H}_2\text{O}$ ($M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$ and Cu(II) , $x = 0$ or 1.75) was studied in order to investigate the effect of the presence of an oxygen heteroatom in the amine ring and on

*e-mail: cavalheiro@dq.ufscar.br

parameters such as atomic radius of the metal center and character of coordination (mono or bidentate) on the thermal behavior.

Experimental

DTC synthesis and characterization

The Mor ammonium salt was obtained by the reaction between the carbon disulfide and morpholine, in the presence of ammonium hydroxide^{22,25}, in an ethanol/water 1:1 (v/v) reaction media. The white solid thus obtained was washed with cold ethanol and then crystallized by dissolving in water, followed by addition of ethanol. The solution was frozen and the white needle crystals formed were dried in a vacuum oven at 50°C for 8 h and characterized by vibrational spectroscopy and elemental analysis. The metal complexes were obtained by direct reaction of the DTC ammonium salt and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. The resulting precipitates were filtered off, washed with water and then with ethanol. Finally they were dried and characterized as above.

Buffer solutions

The McIlvaine buffer solutions with ionic strength adjusted to 0.50 mol dm^{-3} (NaClO_4) were prepared according to the procedure described by Elving et al²⁶. The pH values of these buffers were measured with a glass electrode calibrated with solutions of ionic strength 0.50 mol dm^{-3} (NaClO_4), hydrogen ion concentration 1.00×10^{-2} and $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ (HClO_4), corresponding to pH 2.00 and 4.00, respectively²⁷.

Equipment

Characterization of the complexes was performed by IR vibrational spectroscopy (KBr pellets) with a Bomem MB-102 spectrophotometer; flame atomic absorption spectroscopy was carried out in an Hitachi Z-8100 spectrophotometer and C,N,H contents were determined by elemental analysis using a Fisons EA 1108 CNHS-O instrument.

Thermogravimetric (TG) curves were recorded in a DuPont 9900 thermoanalyser coupled with a TGA 951 Thermogravimetric Module under a gas flow of $1.67 \text{ cm}^3 \text{ s}^{-1}$ (N_2 or air), in a platinum crucible, at $0.167 \text{ }^\circ\text{C s}^{-1}$ heating rate and using samples of about 7 mg of compound at atmospheric pressure. The differential scanning calorimetric (DSC) curves were recorded in a DuPont 9900 thermoanalyser coupled with a DSC 910 Calorimetric Module under a gas flow of $1.67 \text{ cm}^3 \text{ s}^{-1}$ (N_2 or air), in

covered aluminum pans, at $0.167 \text{ }^\circ\text{C s}^{-1}$ heating rate and using samples of about 5 mg of compound at atmospheric pressure. The cell was previously calibrated for temperature and energy using indium metal (99.9+%) as standard.

Intermediates of thermal decomposition process were obtained in an oven at the same temperature and atmosphere that they appeared in the TG curves. After 15 min they were cooled down and kept in a desiccator under vacuum. The X-ray patterns of the crystalline residues were recorded in a VEB-Karl Zeiss Jena URD6 diffractometer. The results were compared with standard data from the International Centre for Diffraction Data, for characterization.

A diode-array Hewlett-Packard HP 8451A spectrophotometer and quartz cells, 1.00 cm path length, were used in the spectrophotometric measurements. The pH values were measured with a Corning IA 250 coupled to a Metrohm EA 121 combined glass electrode and X-ray diffraction patterns of intermediate and final products of thermal decomposition, with an HZG4-Karl Zeiss Jena diffractometer.

Procedure for pKa determination

The spectrophotometric method used for pKa determination was described earlier²². All the spectrophotometric measurements were carried at $25.0 \pm 0.1 \text{ }^\circ\text{C}$, using buffered solutions as blanks. Stock NH_4Mor solutions ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) were used in the preparation of working solutions, with concentration ranging from 1.70×10^{-5} to $8.40 \times 10^{-5} \text{ mol dm}^{-3}$ at pH 2.66 and $5.22 \text{ NH}_4\text{Mor}$ solution $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ NH_4Mor solution was used in the determination of the maximum absorption wavelength, of the acidic and basic forms, in pH ranging from 2.87 to 5.15. In order to minimize the decomposition of the compounds, the solutions were prepared directly in the cells. Thus an appropriate volume of the stock solution of NH_4Mor was transferred with an automatic pipette and introduced in the buffer solution reaching a final volume of 3.00 cm^3 .

Results and Discussion

The prepared compounds are listed in Table 1 and the formulae given are in agreement with elemental analyses and thermogravimetric data. The ligand structure is presented in Figure 1 which also shows the structure of the 5 membered pyrrolidinedithiocarbamate (Pyr) and 6 membered piperidinedithiocarbamate (Pip) cyclic derivatives whose pKa and thermal decomposition data are compared to those of Mor. The unique hydrated complex was $[\text{CoMor}_2] \cdot 1.75\text{H}_2\text{O}$. The presence of a non-stoichiometric amount of water weakly bonded to the

complex is in agreement with previous observations for Co-DTC complexes²⁴ and is confirmed by a mass loss starting at the beginning of the TG curves and by an endothermic process in DSC (Figures 2 and 3).

All the complexes showed a split IR absorption band around 1000 cm⁻¹, indicating that the ligand presents a monodentate behavior according to Sharma⁶ and Nakamoto²⁸.

The characteristic C–N stretching vibrational mode is observed at 1493–1415 cm⁻¹ and is less intense than that

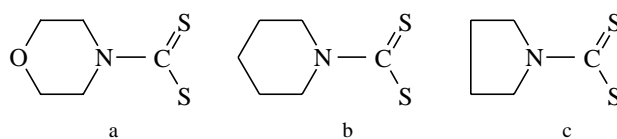


Figure 1. Structures of cyclic dithiocarbamates derived from (a) Morpholine, (b) Piperidine and (c) Pyrrolidine.

observed for alkyl DTC derivatives due to the low double bond character caused by the rigid ring system²⁹. The $\nu(\text{C-O-C})$ vibration³⁰ in the ring appears around 1110 cm⁻¹.

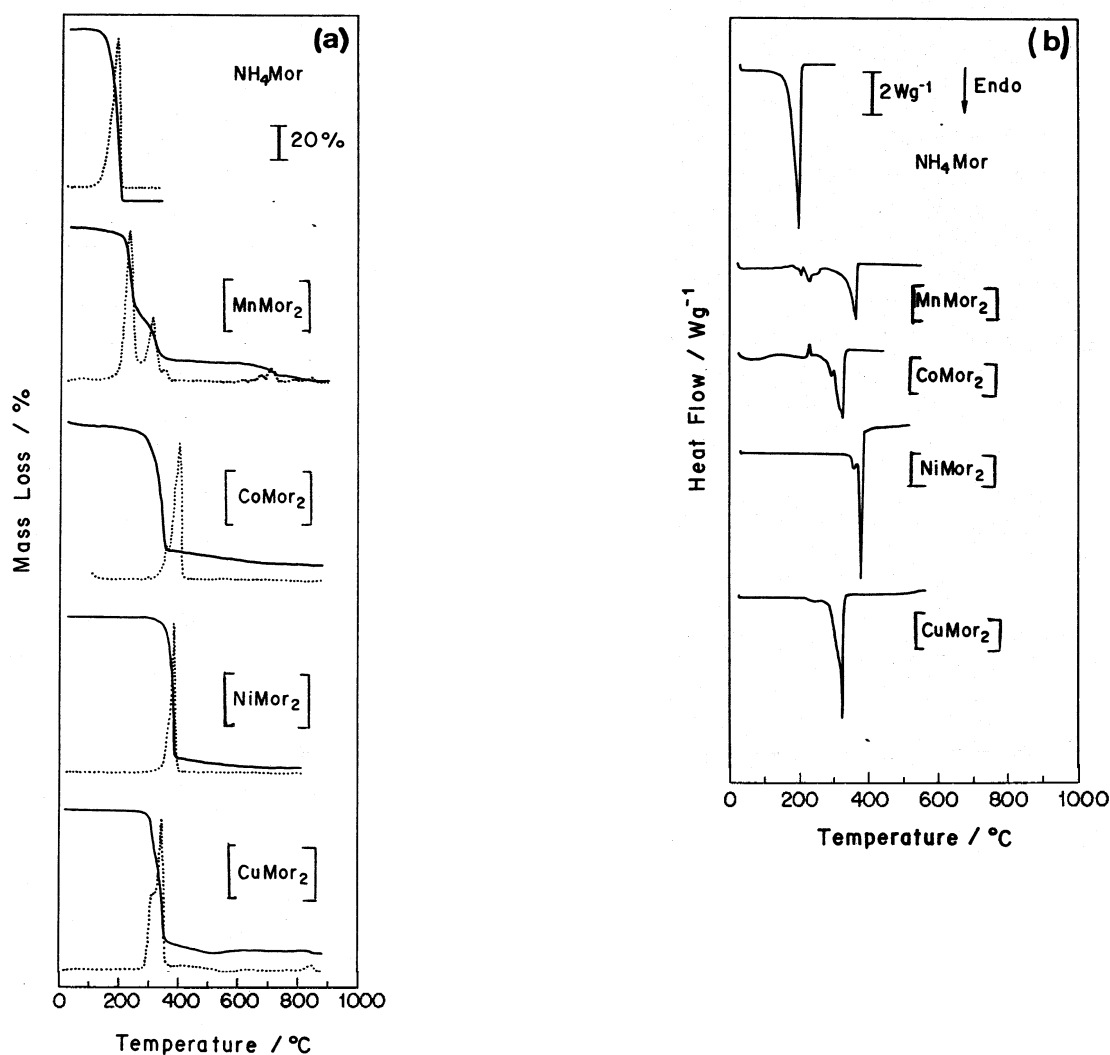


Figure 2. TG (solid)/DTG(dashed) (a) and DSC (b) curves under nitrogen flow of 100 cm³ min⁻¹, other conditions as in the text.

Table 1. Percentages of carbon, hydrogen and nitrogen found and (calculated) and the main infrared bands (cm⁻¹) for the morpholinedithio-carbamates studied in this work.

Compound	Metal	C	H	N	$\nu(\text{C-S})$	$\nu(\text{C-O-C})$	$\nu(\text{C-N})$	$\nu(\text{M-S})$
NH ₄ Mor	-	33.3(32.4)	6.7(6.6)	15.5(15.2)	983,1018	1102	1415	-
MnMor ₂	14.0(14.5)	30.8(31.6)	4.1(4.2)	7.2(7.4)	1018,1024	1110	1471	372
CoMor ₂ ·1.75H ₂ O	12.8(14.7)	28.9(28.9)	4.0(4.7)	6.7(6.8)	1000,1015	1110	1484	359
NiMor ₂	15.3(15.3)	31.0(31.3)	4.1(4.2)	7.3(7.3)	1000,1018	1110	1493	385
CuMor ₂	16.7(16.4)	30.4(30.9)	4.1(4.2)	7.2(7.4)	1000,1018	1109	1483	340

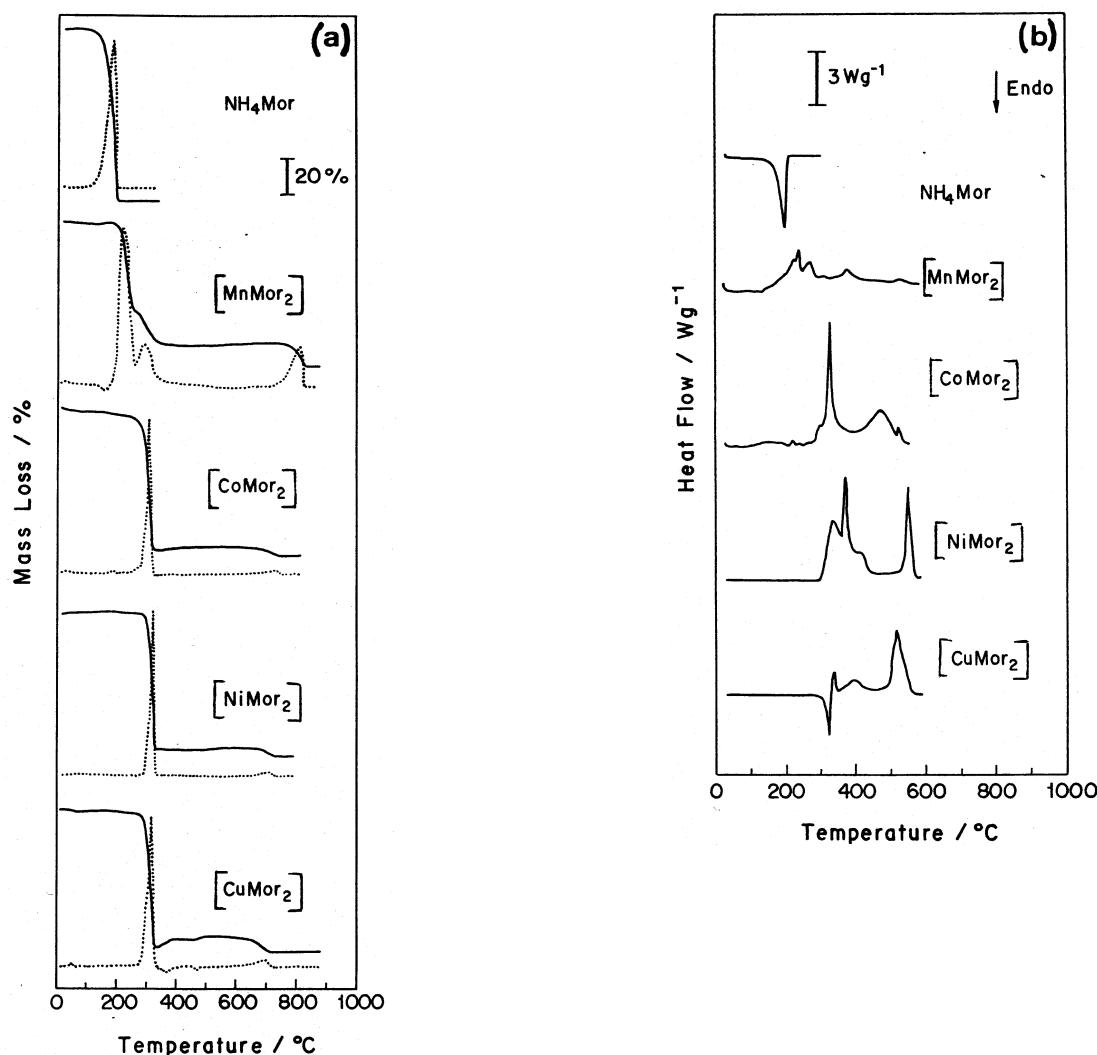


Figure 3. TG (solid)/DTG(dashed) (a) and DSC (b) curves under air flow of $100 \text{ cm}^3 \text{ min}^{-1}$, other conditions as in the text.

pKa determination

The use of diode array data for pKa determination is convenient since the decomposition of DTC occurs very fast in acidic media¹⁸⁻²¹. The decomposition rate depends on the amine substituents. The procedure considers that the total absorbance at a given wavelength is due to the sum of the absorbances of the protonated (HMor) and free (Mor⁻) forms of the DTC:

$$A_A = \epsilon_{A,\text{HMor}}[\text{HMor}] + \epsilon_{A,\text{Mor}^-}[\text{Mor}^-] \quad (1)$$

$$A_B = \epsilon_{B,\text{HMor}}[\text{HMor}] + \epsilon_{B,\text{Mor}^-}[\text{Mor}^-] \quad (2)$$

where, A_A and A_B are the absorbances in the wavelengths A and B, respectively, $\epsilon_{A,\text{HMor}}$ and $\epsilon_{A,\text{Mor}^-}$ are the molar absorptivities of the protonated and free forms in the wavelength A, and $[\text{HMor}]$ and $[\text{Mor}^-]$ are the concentrations of the protonated and free forms, respectively. The absorptivity coefficients can be obtained from the slopes of

A vs $[\text{Mor}^-]$ plots, at the maximum wavelengths in acidic and basic media. On solving equations (1) e (2), it is possible to determine the $[\text{Mor}^-]/[\text{HMor}]$ ratio. Then, measuring the absorbances at different pH values the pKa can be determined by the Henderson-Hasselbach equation:

$$\text{pK} = \text{pH} - \log \frac{[\text{Mor}^-]}{[\text{HMor}]} \quad (3)$$

The maximum wavelength of the protonated HMor form was observed at 286 nm. The free form presented two maxima at 264 and 288 nm. For best resolution, 264 nm (basic, $\epsilon = 2.14 \times 10^3 \text{ cm}^{-1} \text{ mol dm}^{-3}$) and 286 nm (acidic, $\epsilon = 2.06 \times 10^3 \text{ cm}^{-1} \text{ mol dm}^{-3}$) were used in the pKa determination. The results are summarized in Table 2 and $\text{pK} = 3.56 \pm 0.57$ was obtained.

Values of pKa around 5.20 were previously reported, using polarographic³¹ and spectrophotometric³² methods, under different ionic strengths.

Table 2. pKa determination results for HMor ($I = 0.50 \text{ mol dm}^{-3}$, 25°C).

pH	absorbance		[Mor ⁻]/[HMor]	pKa
	264 nm	286 nm		
2.62	0.126	0.134	0.267	3.20
3.25	0.317	0.339	0.341	2.78
3.73	0.463	0.492	0.980	3.74
4.76	0.615	0.643	1.75	4.52
			average	3.56 ± 0.57

An important point in favor of the present results are the changes in spectral shape when the pH is changed from 2.75 to 5.20 (Figure 4). According to Vandebek et al²⁰, the acidic form of a DTC presents only one peak in UV, while the basic form presents two peaks. Figure 4 shows that from pH 3.30 two peaks are clearly observed evidencing the presence of a significant amount of the basic form. If the pKa was 5.20, the ratio [Mor⁻]/[HMor] = 0.02 at pH 3.52 and only one peak should be observed at UV spectra at such conditions.

Decomposition kinetics

The decomposition of NH_4Mor was followed by the absorbance decay of the peak at 286 nm at different pH values. The $\ln A/A_0$ vs. time plots showed a linear dependence suggesting a pseudo-first order kinetics with slope equal to k_{ap} .

The decomposition of dithiocarbamates was investigated by Chakrabarty and co-workers¹⁸⁻²¹. According to these authors the rate of decomposition in basic media is dependent of the pH ($[\text{H}^+] \ll K_a$) but in sufficiently acidic solutions ($[\text{H}^+] \gg K_a$) it becomes constant ($k_{\text{ap}} \approx k_{\text{lim}}$), according to:

$$k_{\text{ap}} = k_{\text{lim}} \left(\frac{[\text{H}^+]}{[\text{H}^+] + K_a} \right) \quad (4)$$

in which k_{ap} is the apparent rate constant from $\ln A/A_0$ vs. time plots, k_{lim} is the limiting rate constant at low pH and K_a is the acidic dissociation constant.

The results obtained for Mor⁻, in Table 3, and show that the presence of the oxygen in the morpholine ring makes it less stable than the analogous piperidinedithiocarbamate ($t_{1/2\text{lim}} = 10 \text{ s}$) and the 5 membered ring pyrrolidine derivative ($t_{1/2\text{lim}} = 1620 \text{ s}$)²².

Thermal decomposition of solid state complexes

The thermal processes, residues formed, mass losses and temperature ranges observed in each step of the TG/DTG and DSC curves are given in Table 4. When crystalline intermediates were obtained they have been characterized on the basis of their X-ray diffraction patterns, compared with literature data³³ (see Table 5). The TG/DTG and DSC curves are presented in Figure 2 under N_2 and in Figure 3 under air.

a) Thermal decomposition under nitrogen

The ammonium salt showed complete volatilization between $105\text{-}205^\circ\text{C}$, without residue on the crucible. IR spectra of the original and condensed salts confirmed the sublimation phenomena.

Presence of hydration water in $[\text{CoMor}_2]$ is confirmed in TG/DTG and DSC experiments. The TG curves of the metal complexes showed decomposition in a single step, except for $[\text{MnMor}_2]$. The first products of thermal

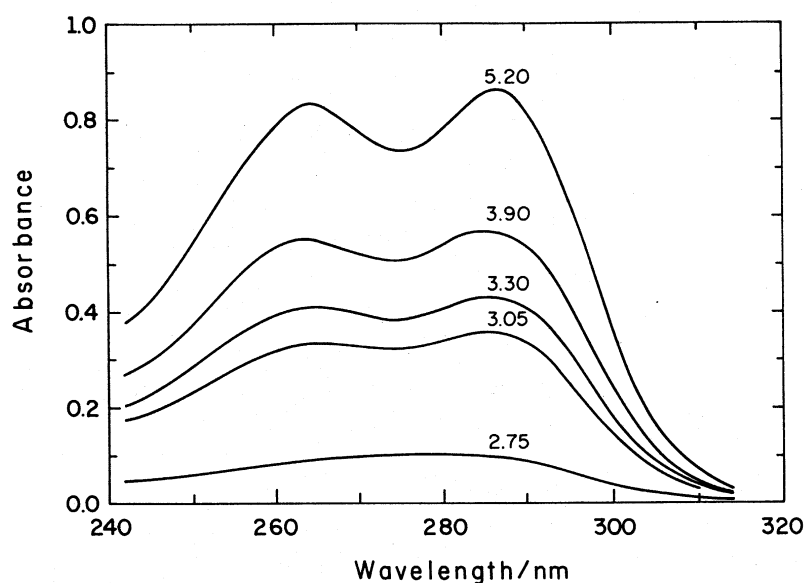


Figure 4. Changes in the spectral shape of a $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ HMor solution, when the pH is changed from 2.75 to 5.20.

Table 3. NH₄Mor decomposition kinetic data at different pH values in ionic strength 0.50 mol dm⁻³ (NaClO₄).

pH	[H ⁺] / 10 ⁵ mol L ⁻¹	k _{ap} / 10 ³ s ⁻¹	t _{1/2} / s	k _{lim} / s ⁻¹	t _{1/2 lim} / s
3.73	18.6	41.0	17	0.20	3.5
4.30	4.90	6.70	103	0.11	6.6
5.25	0.62	0.94	0737	0.11	6.2
5.94	0.12	0.23	2970	0.15	4.8
average				0.14±0.04	5.3±1.2

Table 4. Thermal degradation data of the compounds in nitrogen and air atmospheres, in thermogravimetry, showing the thermal process, the interval of temperature (ΔT), mass losses (Δm) obtained (obt) and calculated (clc), or residue (res) and by differential scanning calorimetry, indicating the temperature of the peak (T), the nature of the endothermic (endo) or exothermic (exo) process.

Thermal Process	ΔT / °C (TG)	obt	Δm / % clc	DSC Data T / °C
<i>N₂ Atmosphere</i>				
NH ₄ Mor(s) → NH ₄ Mor(g)	105-205	100 ^a	100	198 (endo)
[MnMor ₂] → Mn(SCN) ₂ + CR ^d	44-270	50.0 ^b	–	210, 233 (endo)
Mn(SCN) ₂ → MnS ₂ + MnS + CR ^d	270-525	24.1 ^b	–	365 (endo)
MnS ₂ + MnS + CR ^d _{excess} → MnS + CR ^d	636-739	17.5 ^b	–	–
MnS + CR ^d → Mn	739-900	14.1 ^b	14.5	–
[CoMor ₂]·1.75H ₂ O → CoMor ₂ + 1.75 H ₂ O(g)	40-243	7.1 ^a	7.6	72 (endo), 229 (exo)
[CoMor ₂] → CoS + CR ^d	243-360	33.5 ^b	–	294, 326 (endo)
CoS + CR ^d → CoS + Co	360-700	23.8 ^b	–	–
[NiMor ₂] → NiS + CR ^d	285-400	21.3 ^b	–	357, 380 (endo)
NiS + CR ^d → Ni	400-750	15.8 ^b	15.3	–
[CuMor ₂] → Cu _{1.8} S ^c	266-500	20.6 ^b	21.3	321 (endo)
Cu _{1.8} S → Cu _{1.92} S ^c	500-750	21.8 ^b	21.0	–
Cu _{1.92} S → Cu ₇ S ₄ ^c	750-870	20.2 ^b	21.0	–
<i>Air Atmosphere</i>				
NH ₄ Mor(s) → NH ₄ Mor(g)	105-200	100 ^a	100	198 (endo)
[MnMor ₂] → MnSO ₄ + Mn _x O _y	180-352	33.8 ^b	–	225, 240, 275 (exo), 300, 333 (endo)
MnSO ₄ + Mn _x O _y → Mn ₃ O ₄	750-830	20.2 ^b	20.1	–
[CoMor ₂]·1.75H ₂ O → CoMor ₂ + 1.75 H ₂ O(g)	40-243	7.2 ^a	7.6 ^b	70 (endo)
[CoMor ₂] → CoO ^c + Co ₂ O ₃ ^c	243-450	39.0 ^b	–	330 (exo)
CoO + Co ₂ O ₃ → Co ₃ O ₄ ^c	600-747	21.6 ^b	21.0	–
[NiMor ₂] → NiS ^c	285-335	24.8 ^b	23.7	338 (exo)
NiS → NiO ^c	645-750	21.2 ^b	19.5	–
[CuMor ₂] → CuS + CuO	270-600	23.8 ^b	–	323 (endo), 338 (exo)
CuS + CuO → CuO ^c	600-700	20.9 ^b	20.5	–

^arelative to mass loss; ^brelative to residue; ^ccharacterized by X-ray diffraction pattern – see Table 5; ^dCR = carbonaceous residue.

decomposition are the corresponding sulfides and/or carbon. At higher temperatures the presence of carbon produced metallic Mn, Co and Ni and Cu₂S for the respective DTC. The DSC peaks were in agreement with TG results.

Heating [MnMor₂] in a glycerin bath at 270°C in a 20 cm long glass tube led to the condensation of a white substance, whose IR spectrum suggested the presence of Mor⁻ bands and whose decomposition is probably related with the loss of dithiocarbamate.

Although some DTG and DSC curves presented shoulders suggesting that the decomposition occurs in more

than one step, stoichiometric calculations do not lead to the conclusion that decomposition proceeds *via* a thiocyanate intermediate. This is in agreement with previous findings for piperidinedithiocarbamate^{23,24}, also a 6-membered amine ring derivative.

b) Thermal decomposition under air

Under air [CoMor₂]·1.75H₂O, [NiMor₂] and [CuMor₂] decomposed in a single step, according to the TG results presented in Figure 3. Depending on the metallic center in the complex, sulfides (Cu, Ni), oxides (Cu, Co) or sulfate (Mn) are the main products of thermal decomposition.

Table 5. X-ray data for the residues at different temperatures compared with literature standards³³.

Compound	residue at/ standard	d / Å										
[CuMor ₂]	600°C (N ₂)	3.21	3.01	2.78	2.14	1.97	1.79	1.68	1.40	-	-	-
	Cu _{1.8} S ^a	3.21	3.01	2.78	2.14	1.97	1.81	1.68	1.39	-	-	-
	750°C (N ₂)	3.26	3.04	2.96	2.83	2.30	2.27	2.00	1.97	1.88	1.77	1.70
	Cu _{1.92} S ^a	3.26	3.04	2.92	2.82	2.31	2.26	2.00	1.97	1.88	1.77	1.71
	800°C (N ₂)	3.22	2.78	2.75	2.61	2.14	2.00	1.97	-	-	-	-
	Cu ₇ S ₄ ^a	3.22	2.78	2.77	2.62	2.17	1.98	1.96	-	-	-	-
[NiMor ₂]	750°C (air)	2.52	2.32	1.86	1.58	1.50	1.41	1.38	-	-	-	-
	CuO ^a	2.54	2.34	1.87	1.59	1.51	1.42	1.38	-	-	-	-
	400°C (N ₂)	2.98	2.60	1.99	1.72	1.05	-	-	-	-	-	-
	NiS ^a	2.97	2.58	1.97	1.71	1.05	-	-	-	-	-	-
	370°C (air)	2.98	2.60	1.98	1.71	-	-	-	-	-	-	-
	750°C (air)	2.41	2.09	1.48	1.26	-	-	-	-	-	-	-
[CoMor ₂]	NiO ^a	2.41	2.09	1.48	1.26	-	-	-	-	-	-	-
	500°C (N ₂)	3.26	2.83	2.62	2.32	2.26	1.77	1.60	1.58	1.38	-	-
	Co ₂ O ₃ ^a	3.21	2.87	-	2.33	-	1.78	-	1.57	-	-	-
	CoO ^a	-	-	2.62	-	2.27	-	1.61	-	1.37	-	-
	750°C (air)	2.85	2.43	2.02	1.56	1.43	-	-	-	-	-	-
	Co ₃ O ₄ ^a	2.86	2.44	2.02	1.56	1.43	-	-	-	-	-	-

a- data from reference 33.

Table 6. Starting decomposition temperatures obtained from TG data for Mor complexes compared with Pyr and Pip analogues.

metal	starting decomposition temperature / °C		
	Mor	Pip ^a	Pyr ^a
<i>N₂ atmosphere</i>			
Co(II)	243 ^b	232 ^b	267 ^b
Ni(II)	285	272 ^b	284
Cu(II)	266	215 ^b	258 ^b
<i>Air atmosphere</i>			
Co(II)	243 ^b	211 ^b	256 ^b
Ni(II)	285	297 ^b	296
Cu(II)	270	205 ^b	240 ^b

a - data from reference 24; b - after dehydration.

These compounds are converted to the respective oxides at higher temperatures (see Table 4).

The manganese complexes showed a mass gain before decomposition. This is probably related to the addition of an oxygen atom to the complex, according to elemental analysis data, which may be related to the presence of sulfate as decomposition product in this case.

TG/DTG and DSC results confirmed the presence of water in [CoMor₂]. The endothermic process at 310 °C in DSC of [CuMor₂] suggests an initial reduction of the metal at the beginning of the decomposition process. Other DSC peaks were in agreement with TG/DTG data.

In Table 6 starting decomposition temperatures are summarized for some [MMor] complexes (M = Co(II), Ni(II) and Cu(II)) in comparison with Pyr and Pip analogue complexes. These data suggest that the presence of the oxygen atom in the amine ring makes the Mor derivatives thermally more stable than Pip analogues. This should be related with the oxygen tendency to concentrate the electronic density thereby weakening the N-C bond in

relation to Pip. The less tense 5-membered Pyr ring results in complexes more stable than the corresponding Mor and Pip complexes.

Conclusions

The presence of the oxygen as heteroatom in the amine ring makes HMor a stronger acid than the equivalent piperidinedithiocarbamic acid (HPip). The limiting half life ($t_{1/2 \text{ lim}}$) suggests that Mor⁻ is slightly less stable than piperidinedithiocarbamate (Pip) and much less stable than pyrrolidinedithiocarbamate (Pyr)²³.

In all complexes the ligand presented coordination in a monodentate way and [MnMor₂] was the only one that seemed to decompose *via* a thiocyanate intermediate. The starting decomposition temperatures followed the order: Pyr>Mor>Pip for similar metallic complexes²⁴ under both atmospheres.

In relation to the metal, the thermal stability order was: [MnMor₂] < [CoMor₂] < [NiMor₂] > [CuMor₂], showing that the smaller the metallic radius, the more stable the complex, which is in agreement with previous observations^{23,24,34}.

References

- Rabbi, M. F.; Finnegan, A.; Al-Hartli, L.; Stong, S.; Roebuck K. A. *Journal of Acquired Immune Deficiency Syndromes and Human Retrovirology* **1998**, *19*, 321.
- Topping, R. M.; Jones, M. M. *Med. Hypothesis* **1989**, *27*, 55.

3. Weuffen, A.; Kewitsch, A. *Arch. Exp. Veterinaarmed.* **1967**, *21*, 1049.
4. Powell, A. K. *Brit. J. Cancer* **1954**, *8*, 529.
5. Hill, J. O.; Chirawongaram, S. *J. Thermal Anal.* **1994**, *41*, 511.
6. Sharma, A. K. *Thermochim. Acta* **1986**, *104*, 339.
7. Magee, R. J.; Hill, J. O. *Rev. Anal. Chem.* **1985**, *8*, 5.
8. Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* **1984**, *54*, 23.
9. Sengupta, S. K.; Kumar, S. *Termochim. Acta* **1984**, *72*, 349.
10. Hill, J. O.; Magee, R. J. *Rev. Inorg. Chem.* **1981**, *3*, 141.
11. Coucovanis, D. *Progr. Inorg. Chem.* **1979**, *26*, 301.
12. Coucovanis, D. *Progr. Inorg. Chem.* **1970**, *11*, 233.
13. Hulanicki, A. *Talanta* **1967**, *14*, 1371.
14. Thorn, G. D.; Ludwig, R. A. *The Dithiocarbamates and Related Compounds*, Elsevier; Amsterdam, 1962.
15. Castro, E. A.; Cortes, R.; Santos, J. G.; Vega, J. C. *J. Org. Chem.* **1982**, *47*, 3774.
16. De-Filippo, D.; Deplano, P.; Devillanova, F.; Trogu, E. F.; Verani G. *J. Org. Chem.* **1973**, *38*, 560.
17. Usatenko, Y. I.; Barkalov, U. S.; Tulypa, F. M. *J. Anal. Chem.-USSR.* **1970**, *25*, 1458.
18. Aspila, K. I.; Chakrabarti, C. L.; Sastri, V. S. *Anal. Chem.* **1973**, *45*, 363.
19. Joris, S. J.; Aspila, K. I.; Chakrabarti, C. L. *J. Phys. Chem.* **1970**, *74*, 860.
20. Vandebek, R. R.; Joris, S. J.; Aspila, K. I.; Chakrabarti, C. L. *Can. J. Chem.* **1970**, *48*, 2204.
21. Aspila, K. I.; Sastri, V. S.; Chakrabarti, C. L. *Talanta* **1969**, *16*, 1099.
22. Cavalheiro, E. T. G.; Chierice, G. O. *J. Braz. Chem. Soc.* **1997**, *8*, 53.
23. Cavalheiro, E. T. G.; Ionashiro, M.; Marino, G.; Breviglieri, S. T.; Chierice, G. O. *J. Braz. Chem. Soc.* **1999**, *10*, 65.
24. Cavalheiro, E. T. G.; Ionashiro, M.; Marino, G.; Breviglieri, S. T.; Chierice, G. O. *Transit. Metal Chem.* **2000**, *25*, 69.
25. Malissa, H.; Schöffman, S. *Mikrochim. Acta* **1955**, *1*, 187.
26. Elving, P. J.; Morkowitz, J. M.; Rosenthal, I. *Anal. Chem.* **1956**, *28*, 1179.
27. Cavalheiro, E. T. G.; Plepis, A. M. G.; Chierice, G. O.; Neves, E. F. A. *Polyhedron* **1987**, *9*, 1717.
28. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 3rd. Ed.; John Wiley; New York, 1977.
29. Preti, C.; Tosi, G.; Zanini, P. *J. Mol. Struct.* **1979**, *53*, 35.
30. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; 5th. Ed.; John Wiley; New York, 1991.
31. Zahradnik, R.; Zuman, P. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1132.
32. de Filippo, D.; Preti, C. *Gazz. Chim. Ital.* **1965**, *95*, 707.
33. International Centre for Diffraction Data. Power Diffraction File (CD-ROM). Newton Square, ICDD, 1994.
34. Breviglieri, S. T.; Cavalheiro, E. T. G.; Chierice, G. O. *Termochim. Acta* **2000**, *25*, 69

Received: March 24, 2000

Published on the web: April 20, 2001

FAPESP helped in meeting the publication costs of this article.