Thermoanalytical and Solution Stability Studies of Hexamethylenedithiocarbamates

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Estudos termogravimétricos e calorimétricos exploratórios diferenciais de hexametilenoditiocarbamatos de níquel(II), cobre(II), zinco(II) e cádmio(II) foram realizados sob atmosferas dinâmicas de ar e nitrogênio, para avaliar as etapas e os produtos de decomposição térmica. Esses produtos, quando cristalinos, foram caracterizados por difratometria de raios X, sendo predominantemente constituídos por sulfetos e óxidos metálicos sob N2 e ar, respectivamente. Usando espectrofotometria na região do ultravioleta, também foram determinados o pK a = 3,6 ± 0,2 para o ácido hexametilenoditiocarbâmico em força iônica igual a 0,50 mol dm-3 (KCl) a 25,0 °C e os parâmetros cinéticos de decomposição em diferentes valores de pH (k lim = 2,21 × 10-2 s-1 e t½ lim = 156 s).

Thermogravimetric and differential scanning calorimetric investigation of the thermal behavior of nickel(II), copper(II), zinc(II) and cadmium(II) hexamethylenedithiocarbamates were performed under nitrogen and air atmospheres in order to investigate the steps and products of thermal decomposition. When obtained in a crystalline form, the decomposition products were identified by their X-ray diffraction patterns. Metal sulfides and oxides were the major residues under nitrogen and air atmospheres, respectively. Spectrophotometric measurements in the ultraviolet region were used to estimate the pK a = 3.6 ± 0.2 for the hexamethylenedithiocarbamic acid at 0.50 mol dm-3 ionic strength (KCl) at 25.0 °C and the kinetic parameters of decomposition at different pH values (k lim = 2.21 × 10-2 s-1 and t½ lim = 156 s).

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

Introduction

Dithiocarbamates (DTC) are products of the reaction between a primary or secondary amine and carbon disulfide in basic media. Their versatility and applicability was discussed by Kitson.1 The interest in the solution stability of dithiocarbamates has been renewed by the utilization of such compounds as coadjuvants in the treatment of AIDS,2,3 but they have also been suggested for tuberculosis4 and cancer5 treatment in the past. These applications demand enough chemical stability for an effective action in the biological medium.

The applications of this class of compounds are not limited to medicine and their use in agriculture, industry, analytical and organic chemistry, as well as their physicochemical properties, are summarized in several review articles.6-15 From these works it is known that dithiocarbamates obtained from cyclic amines are more stable than the aliphatic derivatives.

The stability of dithiocarbamates in solution is strongly dependent on the pH, as discussed by several authors.16-22 However, it was the work of Chakrabarti and co-workers19-22 that led to the proposition of a decomposition intermediate whose stability is related to the presence of a water molecule in its structure.

Considering that the decomposition of dithiocarbamates is very fast in acidic media, a spectrophotometric method based on diode-array measurements has been proposed23 in order to reach 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 on the thermal decomposition of such compounds has also been presented.24,25

Hexamethylenedithiocarbamate (hex) is a cyclic DTC derived from hexamethyleneimine (homopiperidine), a
seven member heterocyclic amine, whose structure is represented in Figure 1.

Figure 1. Structure of the hexamethylenedithiocarbamate.

Among many other applications, hex complexes have widely been used in the determination of several metals using different strategies and techniques for pre-concentration. Examples of such applications, presented during the last 35 years, include the recent description of the profitable use of Co(hex)$_3$, Fe(hex)$_3$ and its mixtures with Fe$_2$O$_3$•xH$_2$O and Pb(hex)$_2$ as a colloidal precipitate collector in the flotation preconcentration of Cd, Cu, Fe, Ni, Pb, Zn, Ti, Cr and Mn, allowing determinations at the ng dm$^{-3}$ range in several water samples.

These complexes have also been used to pre-concentrate metal ions in columns. After this step, the complexes are eluted and inserted in HPLC systems, allowing separations and simultaneous quantifications. They have also been employed in separation and co-precipitation and in the less recent applications with solid and liquid phase extractions followed by determination by atomic spectroscopic techniques of several elements.

Studies regarding the standard enthalpy of formation of hexamethyleneaminium hexamethylenedithiocarbamate, dye-sensitized photolysis and crystal structures of ligand and complexes can also be found.

Thermal analysis of mixed-ligand nickel hexamethylenedithiocarbamate complexes with triphenyl and tributylphosphine, as well as of lanthanide complexes with hexamethylenedithiocarbamate, have been described. Recently, the thermal behavior of the ammonium and hexamethyleneaminium salts of hexamethylenedithiocarbamate was also reported.

The solution stability of the hexamethylenedithiocarbamate proved to be important in medical applications. A representative example is the patent presented by the French Roussel-Uclaf company regarding the use of this DTC as a protector of hepatic cells. The compound is taken orally or by a bloodshot as an alkaline cation salt solution. In addition, the thermal behavior is another important feature in industrial and agricultural application of this dithiocarbamate, as related to thermal stability and residues generated during thermal decomposition.

Despite the importance of the solution and thermal stability for hex applications, few studies regarding these issues have been reported. In the present work, the pK$_a$ value of the hexamethylenedithiocarbamic acid (Hhex) was determined in ionic strength $I = 0.50$ mol dm$^{-3}$ by spectrophotometry in the ultraviolet region, and used to estimate the decomposition rate of hexamethylenedithiocarbamate (hex) at different pH values using a method based on diode-array measurements of the absorbance. Additionally, the thermal behavior of M(hex)$_2$ (M = nickel(II), copper(II), zinc(II) and cadmium(II)) solid state complexes was evaluated, as these compounds are important examples of hex complexes with industrial and agricultural applications.

**Experimental**

All reagents were of analytical grade and used without further purification. The water employed in all experiments was deionized before use.

**Hexamethyleneaminium-hexamethylenedithiocarbamate (HMA-hex) - synthesis and characterization**

The HMA-hex salt was obtained by dissolving 0.4 mol of hexamethyleneimine in 50 dm$^3$ of ethanol/water 1:1 (v/v) in an erlenmeyer. The mixture was kept in an ice bath and protected from the light. Nitrogen was bubbled into the solution for 5 min and then 0.2 mol of carbon disulfide was slowly added to the reaction mixture. The white solid thus obtained was filtered, washed with cold ethanol and then dissolved in a minimum amount of ethanol/water 1:1 (v/v) at 35 °C, protected from the light. The solution was frozen and the white needle-like crystals were dried in a vacuum oven at 35 °C for 8 h and characterized as:

**Hexamethylenedithiocarbamate complexes - synthesis and characterization**

The metal complexes were obtained by direct reaction of the HMA-hex solution and CdCl$_2$•2H$_2$O, CuCl$_2$•H$_2$O, NiCl$_2$•6H$_2$O and ZnCl$_2$ solutions in a glove bag (Cole-Parmer, USA) under N$_2$. The resulting precipitates, with characteristic colors, were filtered off, washed with water and then with ethanol. They were finally dried in a vacuum oven at 35 °C for 8 h and characterized as:
**Buffer solutions**

The McIlvaine buffer solutions with ionic strength adjusted to 0.50 mol dm\(^{-3}\) (KCl) were prepared according to the procedure described by Elving et al.\(^8\)\(^7\) The pH values of these buffers were accurately measured with a glass electrode previously calibrated with KCl solutions of ionic strength 0.50 mol dm\(^{-3}\) and hydrogen ion concentration 1.00 \(\times\) 10\(^{-2}\) and 1.00 \(\times\) 10\(^{-4}\) mol dm\(^{-3}\) (HClO\(_4\)), corresponding to pH 2.00 and 4.00, respectively.\(^8\)\(^8\)

**Equipment**

The characterization of the complexes was performed by IR vibrational spectroscopy (KBr pellets) in a Nicolet 5SXc spectrophotometer. Flame atomic absorption spectroscopy was carried out in a 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 thermoanalyzer coupled with a TGA 951 Thermogravimetric Module, under a gas flow of 90 dm\(^3\) min\(^{-1}\) (N\(_2\) or air) in a platinum crucible. A heating rate of 10 °C min\(^{-1}\) and samples of about 7 mg at atmospheric pressure were employed. The differential scanning calorimetric (DSC) curves were recorded in a DuPont 9900 thermoanalyzer coupled with a DSC 910 Calorimetric Module under a gas flow of 90 dm\(^3\) min\(^{-1}\) (N\(_2\) or air), in covered aluminum pans with a central pin hole, at a heating rate of 10 °C min\(^{-1}\) and using samples of about 5 mg at atmospheric pressure. The cell was previously calibrated for temperature and energy (\(\Delta H\)) using indium metal (99.9+%) as standard.

Intermediates of the thermal decomposition process were generated in an oven at the same temperature and atmosphere in which they appeared in the TG curves. After 15 min of heating, 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.\(^8\)\(^9\)

**Procedure for pK\(_a\) determination**

The spectrophotometric method used for pK\(_a\) determination was described earlier.\(^2\)\(^,\)\(^9\)\(^0\) All the spectrophotometric measurements were carried out at 25.0 ± 0.1 °C, using the buffered solution as a blank. Stock HMA-hex solutions (1.0 \(\times\) 10\(^{-2}\) mol dm\(^{-3}\)) were used in the preparation of working solutions, with concentrations ranging from 3.34 \(\times\) 10\(^{-3}\) to 1.67 \(\times\) 10\(^{-6}\) mol dm\(^{-3}\) in pH 2.13 and 8.40. A 1.0 \(\times\) 10\(^{-4}\) mol dm\(^{-3}\) HMA-hex solution was used in the determination of the maximum absorption wavelength of the acidic and basic forms, in pH ranging from 2.78 to 4.10. In order to minimize the decomposition of the compounds, the solutions were prepared directly in the cell, by adding an appropriate volume of the stock solution of HMA-hex to the buffer solution and reaching a final volume of 3.00 dm\(^3\).

**Results and Discussion**

The products are listed in Table 1 and the formulae given are in agreement with elemental analyses and thermogravimetric data. The hex structure is presented in Figure 1. All complexes are anhydrous. The split IR absorption band around 1000 cm\(^{-1}\) indicated that the ligand presents a monodentate behavior in Cd(hex)\(_2\) and Zn(hex)\(_2\), while a single absorption band in this region suggests a bidentate behavior in Ni(hex)\(_2\) and Cu(hex)\(_2\), according to Sharma\(^7\) and Nakamoto.\(^9\)\(^1\) This is in total agreement with our previous findings for other cyclic DTC complexes with the same metal cations.\(^2\)\(^,\)\(^2\)\(^5\)\(^,\)\(^9\)\(^0\)

The characteristic C–N stretching vibrational mode is observed at 1474-1503 cm\(^{-1}\) and is less intense than that observed for alkyl DTC derivatives due to the low double bond character caused by the rigid ring system.\(^9\)\(^2\)

| Compound(color) | Metal | C     | H     | N     | \(\nu\)(C-N) | \(\nu\)(C-S) |
|----------------|-------|-------|-------|-------|--------------|--------------|
| HMA-hex(white) | -     | 56.8 (56.9) | 9.89 (9.55) | 9.75 (10.2) | 1474         | 956,975      |
| Ni(hex)\(_2\)(green) | 13.3 (14.4) | 40.2 (41.3) | 5.84 (5.94) | 6.56 (6.88) | 1503         | 980          |
| Cu(hex)\(_2\)(brown) | 14.2 (15.4) | 41.2 (40.8) | 5.93 (5.87) | 6.77 (6.80) | 1500         | 985          |
| Zn(hex)\(_2\)(white) | 15.9 (15.8) | 41.0 (40.6) | 5.99 (5.84) | 6.85 (6.77) | 1485         | 959,982      |
| Cd(hex)\(_2\)(white) | 23.1 (24.4) | 35.8 (36.5) | 5.16 (5.25) | 5.94 (6.08) | 1485         | 959,979      |
**pKₐ determination**

The use of diode array data for pKₐ determination is convenient, since the decomposition of DTC is very fast in acidic media. 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 (Hhex) and free (hex) forms of the DTC:

\[ A_A = \varepsilon_{A,Hhex}[Hhex] + \varepsilon_{A,hex}[hex] \]  
\[ A_B = \varepsilon_{B,Hhex}[Hhex] + \varepsilon_{B,hex}[hex] \]

in which \( A_A \) and \( A_B \) are the absorbances in the wavelengths \( A \) and \( B \), respectively, \( \varepsilon_{A,Hhex} \) and \( \varepsilon_{A,hex} \) are the molar absorptivities of the protonated and free forms in the wavelength \( A \), and \([Hhex]\) and \([hex]\) are the concentrations of the protonated and free forms, respectively. The absorptivity coefficients can be obtained from the slopes of \( A \) versus \([hex]\) plots, at the maximum wavelengths, in acidic and basic media. On solving equations (1) and (2), it is possible to determine the \([hex]/[Hhex]\) ratio. Then, measuring the absorbances at different pH values, the pKₐ can be determined by the Henderson-Hasselbach equation:

\[ pK_a = pH - \log \frac{[hex]}{[Hhex]} \]

The maximum absorption wavelength of the protonated (Hhex) form was observed at 276 nm. The free form presented two maxima at 260 and 283 nm. For best resolution, 260 nm (basic, \( \varepsilon = 1.22 \times 10^4 \text{ cm}^{-1} \text{ mol dm}^{-3} \)) and 276 nm (acidic, \( \varepsilon = 1.06 \times 10^4 \text{ cm}^{-1} \text{ mol dm}^{-3} \)) were used in the pKₐ determination. The results are summarized in Table 2 and a pKₐ value of 3.6±0.2 was obtained. Values of pKₐ around 3.29 were previously reported using a conventional spectrophotometric method at 25 °C and a 0.01 mol dm⁻³ ionic strength.

**Table 2.** Results of the pKₐ determination for Hhex (I = 0.50 mol dm⁻³, 25 °C)

| pH  | absorbance | [hex]/[Hhex] | pKₐ  |
|-----|------------|--------------|------|
|     | 260 nm     | 276 nm       |      |
| 2.78| 0.445      | 0.713        | 0.246| 3.41 |
| 3.39| 0.551      | 0.696        | 0.854| 3.47 |
| 4.21| 0.735      | 0.741        | 3.59 | 3.65 |
| 4.79| 0.819      | 0.778        | 7.35 | 3.93 |

Mean ± sd* 3.6±0.2

*sd = standard deviation (n=4).

Decomposition kinetics

The decomposition of HMA-hex was followed by the absorbance decay of the 286 nm peak at different pH values. The lnA/A₀ versus time plots showed a linear dependence, suggesting a pseudo-first order kinetics with slope equal to \( k_{app} \).

Chakrabarty and co-workers investigated the decomposition of dithiocarbamates. According to these authors, the rate of decomposition in basic media is dependent on the pH (\( [\text{H}^+]<<K_a \)), but in sufficiently acidic solutions (\( [\text{H}^+]>>K_a \)) it becomes constant (\( k_{app} = k_{lim} \)), according to:

\[ k_{app} = k_{lim} \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_a} \right) \]

in which \( k_{app} \) is the apparent rate constant from the ln A/A₀ versus time plots, \( k_{lim} \) is the limiting rate constant at low pH and \( K_a \) is the acidic dissociation constant.

The results obtained for hex are presented in Table 3. These data led us to conclude that hex presents an intermediate stability between the analogous...
piperidinedithiocarbamate, pip \(t_{1/2} = 10 \text{ s}\) and the 5
membered ring pyrrolidine derivative, pyr \(t_{1/2} = 1620 \text{ s}\). Chakrabati and co-workers attributed this
difference to the ability of pyr and hex to interact with a
water molecule in the decomposition intermediate, due
to the configuration of the 5 and 7 membered rings.

The low stability of the anion in acidic medium can
explain the large deviations between the measurements
in Table 3.

**Table 3.** HMA-hex decomposition kinetic data at different pH values and
at an ionic strength of 0.50 mol dm\(^{-3}\) (KCl)

| pH \([\text{H}^+] / (10^{-3} \text{ mol dm}^{-3})\) | \(k_{ap} / 10^3 \text{ s}^{-1}\) | \(t_{1/2} / \text{s}\) | \(k_{lim} / (10^2 \text{ s}^{-1})\) | \(t_{1/2 \lim} / \text{s}\) |
|---|---|---|---|---|
| 2.10 | 7.94 | 62.87 | 11 | 6.48 | 10.7 |
| 2.75 | 1.78 | 1.98 | 350 | 0.225 | 308 |
| 3.98 | 0.105 | 0.770 | 900 | 0.257 | 270 |
| 4.92 | 0.0120 | 0.880 | 7880 | 1.88 | 36.8 |
| Mean | 2.21 | 156 |

**Thermal decomposition of solid state complexes**

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 under nitrogen and
Table 5 under air dynamic atmospheres. Crystalline
intermediates were characterized by X-ray diffraction
patterns and results were compared with literature data. The IR
spectra of the HMA-hex salt and of the condensed product
confirmed the volatilization phenomena.

Crystalline changes were detected for the copper and
the zinc complexes, represented by endothermic peaks in
the DSC curves in both atmospheres. Melting points
were checked by the use of a capillary tube immersed in a
glycerin bath, in order to differentiate them from the
crystalline changes. X-ray diffraction analysis was
performed in order to characterize the crystalline
residues, when available; otherwise the nature of the
residues has been assigned by stoichiometric
calculations. The results are presented in Table 6 and
are compared with literature data. The thermal behavior
of the complexes is discussed below.

**Thermal decomposition under nitrogen**

Thermoanalytical curves are presented in Figure 3. According
to TG/DTG and DSC data, there is no evidence for the presence of hydration water in the solids. Melting
was observed for Cu(hex)\(_2\), Cd(hex)\(_2\), Ni(hex)\(_2\) and
Zn(hex)\(_2\), and it was confirmed in a capillary glass tube

| Thermal Process | \(\Delta T / ^\circ\text{C}\) | \(\Delta m\%\) | DSC Data |
|---|---|---|---|
| Cd(hex)\(_2\) \(\rightarrow\) Cd(hex)\(_2\) | - | - | 238.9 (endo) |
| Cd(hex)\(_2\) \(\rightarrow\) Cd\(_2\) + CR | 222.8-416.5 | 39.7 | 312.6 (endo) |
| Cd\(_2\) + CR \(\rightarrow\) CdS | 416.5-743.5 | 30.7 | 31.3 - |
| Cu(hex)\(_2\) \(\rightarrow\) Cu(hex)\(_2\) | - | - | 121.0 (endo) |
| Cu(hex)\(_2\) \(\rightarrow\) Cu\(_4\) | - | - | 202.4 (endo) |
| Cu\(_4\) \(\rightarrow\) Cu\(_2\) \(\rightarrow\) Cu(SCN)\(_2\) | 196.2-283.1 | 43.6 | 266.4 (endo) |
| Cu(SCN)\(_2\) \(\rightarrow\) Cu\(_2\) | 283.1-605.6 | 23.2 | 407 (exo) |
| Cu\(_2\) \(\rightarrow\) Cu\(_2\) | 605.6-864.4 | 15.4 | 16.9 - |
| Ni(hex)\(_2\) \(\rightarrow\) Ni(hex)\(_2\) | - | - | 268.0 (endo) |
| Ni(hex)\(_2\) \(\rightarrow\) Ni\(_2\)S\(_2\) | 275.0-400.6 | 26.2 | 334.5 (endo) |
| Ni\(_2\)S\(_2\) \(\rightarrow\) NiS | 600.3-682.0 | 22.3 | 22.0 - |
| Zn(hex)\(_2\) \(\rightarrow\) Zn(hex)\(_2\) | - | - | 156.0 (endo) |
| Zn(hex)\(_2\) \(\rightarrow\) Zn\(_2\) | - | - | 180.7 (endo) |
| Zn\(_2\) \(\rightarrow\) Zn\(_2\) | 218.5-386.4 | 21.5 | 20.8 |

*the mass losses refer to the starting material; \(^\circ\)relative to residue in relation to the starting material; \(^\circ\)characterized by X-ray diffraction pattern – see Table 6; \(^\circ\)CR = carbonaceous residue.
Figure 3. TG (solid)/DTG(dashed) (a) and DSC (b) curves under nitrogen flow of 90 dm$^3$ min$^{-1}$, sample mass ca. 7mg, heating heat 10 °C min$^{-1}$, platinum sample holder (TG/DTG) and aluminum (DSC).

Figure 4. TG (solid)/DTG(dashed) (a) and DSC (b) curves under air flow of 90 dm$^3$ min$^{-1}$, sample mass ca. 7mg, heating heat 10 °C min$^{-1}$, platinum sample holder (TG/DTG) and aluminum (DSC).
test. Zn(hex)$_2$ and Cu(hex)$_2$ apparently melted after a crystalline transition, as suggested by the peak shape and the absence of mass loss associated with the process. XRD measurements were not performed before and after the peak in order to confirm these physical changes.

Sulfides were the main residues around 400 °C, after the decomposition of the complexes. Metallic Cd, Cu and Zn were found in the further decomposition steps of the inorganic residue, while NiS remained stable as the final decomposition product in the temperature range investigated.

Only in the Cu(hex)$_2$ case, Cu(SCN)$_2$ was detected as the intermediate in decomposition, as suggested by Sharma. This is in agreement with previous findings for other cyclic dithiocarbamate derivatives. 23-25,90

### Table 5. Thermal degradation data under air, from thermogravimetry, showing the thermal process, the interval of temperature (ΔT), mass losses (Δm) experimental (exp) and calculated (calc), or residue and from differential scanning calorimetry, indicating the temperature of the peak (T), and the endothermic (endo) or exothermic (exo) nature of the process

| Thermal Process | ΔT / °C | Δm ± % | DSC Data |
|-----------------|---------|--------|----------|
| Cd(hex)$_2$ (s) → Cd(hex)$_2$ (l) | - | - | 238.4 (endo) |
| Cd(hex)$_2$ (l) → CdS | 227-617.8 | 31.3 | 31.2 | 309.6, 416.5 (endo) |
| CdS → ½Cd$_2$SO$_4$ | 680.0-794.6 | 34.0 | 36.5 |
| Cu(hex)$_2$ (s1) → Cu(hex)$_2$ (s2) | - | - | - |
| Cu(hex)$_2$ (s2) → Cu(hex)$_2$ (l) | - | - | 264.5 (endo) |
| Cu(hex)$_2$ (l) → ½Cu$_2$S(CN)$_2$ | 387.9-476.7 | 27.1 | 29.0 | 492.0 (exo) |
| Ni(hex)$_2$ (s) → Ni(hex)$_2$ (l) | - | - | 260.0 (endo) |
| Ni(hex)$_2$ (l) → ½Ni$_2$S$_3$ | 244.4-430.5 | 26.2 | 28.3 | 308.0 (endo), 349.3 (exo) |
| Cu$_2$S(CN)$_2$ → ½Cu$_2$SO$_4$ | 187.2-387.9 | 32.0 | - |
| Cu$_2$O → CuO | 568.4-681.3 | 19.3 | 19.8 |
| Zn(hex)$_2$ (s1) → Zn(hex)$_2$ (s2) | - | - | - |
| Zn(hex)$_2$ (s2) → Zn(hex)$_2$ (l) | - | - | 316.5 (endo), 348.0 (exo) |
| Zn(hex)$_2$ (l) → ZnS | 206.5-380.0 | 23.5 | 22.2 | 316.5 (endo), 348.0 (exo) |
| ZnS → ZnO | 390.6-729.5 | 19.7 | 19.5 | - |

*the mass losses refer to the starting material; *relative to residue in relation to the starting material; *characterized by X-ray diffraction pattern – see Table 6.

### Table 6. X-ray diffraction data for the residues at different temperatures, compared with literature standards

| Compound | residue at/standard | d / Å |
|----------|---------------------|-------|
| Cd(hex)$_2$ | 350 °C (N$_2$) | 3.57 3.35 3.15 2.06 1.39 - - - |
| Cu(hex)$_2$ | 300 °C (air) | 3.24 2.85 - 1.99 1.69 - - - |
| Ni(hex)$_2$ | 400 °C (N$_2$) | 3.12 2.03 1.67 1.35 1.25 1.10 1.03 - |

*a data from reference 89.*
decomposition step and were converted to oxide (Zn) or oxysulfates (Cd and Ni) by further heating of the residue (see Table 5). The detection of oxysulfates as decomposition intermediates is in agreement with previous results.24 The copper complex decomposed in a different way, generating Cu$_4$Si(CN)$_6$, oxysulfate and finally the oxide, according to the X-ray diffraction patterns of the residues.30 Crystalline changes and melting processes were also observed, in agreement with the data obtained under N$_2$ and reported in the previous section.

Results indicated that the following stability order can be established, according to the temperature in which decomposition starts: Ni(hex)$_2$ > Cd(hex)$_2$ > Zn(hex)$_2$ > Cu(hex)$_2$.

Conclusions

The Hhex is the weaker acid when compared to the series of cyclic DTC derived from pyrrolidine, piperidine and hexamethylenamine, respectively 5, 6 and 7-membered aminic rings. The limiting half life ($t_{1/2}^\text{lim}$) suggests that hex is more stable than piperidinedithiocarbamate (pip) and morpholinedithiocarbamate (mor) and much less stable than pyrrolinedithiocarbamate (pyr).23,30

The thermal analytical studies revealed that sulfides were the main residues obtained under nitrogen atmosphere, which were reduced to the elementary metals in the case of the copper(II) and zinc(II) complexes. Oxysulfates were observed in air as intermediates of the decomposition of Ni(hex)$_2$, Cu(hex)$_2$ and Cd(hex)$_2$, while oxides were obtained as final decomposition products. The nickel(II) complex was the most stable in this series.

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