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THERMAL BEHAVIOR OF COPPER(II) PSEUDOHALIDE COMPLEXES CONTAINING BIDENTATE AMINES

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Abstract

Pseudohalide complexes of copper(II) with aliphatic bidentate amines, $[Cu(N_3)_2(N,N\text{-diEten})]_2$ **1**, $[Cu(NCO)_2(N,N\text{-diEten})]_2$ **2**, $[Cu(NCO)_2(N,N\text{-diMeen})]_2$ **3**, $[Cu(N_3)(NCS)(N,N'\text{-diMeen})]_2$ **4** and $[Cu(N_3)(NCO)(N,N\text{-diMeen})]_2$ **5** (N,N-*diEten*=N,N-diethylethylenediamine; N,N-*diMeen*=N,N-dimethyl-ethylenediamine and N,N’-*diMeen* = N,N’-dimethylethylenediamine), were prepared, characterized and their thermal behavior was investigated by TG curves. According to thermal analysis and X-ray diffraction patterns all compounds decomposed giving copper(II) oxide as final product. The mechanisms of decomposition were proposed and an order of thermal stability was established.

Keywords: bidentate amines, copper, infrared spectroscopy, pseudohalide, synthesis, thermal analysis

Introduction

The chemistry of the complexes containing pseudohalide ions is a fascinating branch of chemistry that has been attracting an increasing attention during the recent years [1–3]. The reasons for it are their structural diversity arising from the different coordination modes of the pseudohalides to metallic centers and, in particular, the reactions of azido and cyanato, present at the metal coordination sphere, with other molecule giving new species [4]. In addition, investigation of copper(II) pseudohalide complexes continues to be stimulated by the interest in developing models for copper proteins [5] and also by their magnetic properties [6].

Although some copper(II) coordination compounds have been studied by thermogravimetric technique [7], it is a fact that copper(II) pseudohalide complexes, have been scarcely investigated so far. However, the importance of the thermo-

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gravimetric behavior of metal-pseudohalide compounds, notably of those containing azide and cyanate, relies on the possible application as explosives [8]. In order to fill in this gap and as a part of our ongoing studies of coordination chemistry of copper [9–12], we report herein the preparation of copper(II) pseudohalide complexes. Information concerning the stereochemistry of each complex and the type of coordination of the pseudohalide to copper ion has been investigated by using infrared spectroscopy. Furthermore, compounds such as **4** and **5** having two different pseudohalides simultaneously coordinated to the same metallic centre are very uncommon in literature. To the best of our knowledge, this present study is the first one dealing with a systematic thermal behavior in a series of copper-pseudohalide complexes.

Experimental

Preparation

The complexes $[Cu(N_3)_2(N,N\text{-diEten})]_2$ **1**, $[Cu(NCO)_2(N,N\text{-diEten})]_2$ **2** and $[Cu(NCO)_2(N,N\text{-diMeen})]_2$ **3** were prepared as previously described [9–11]. For these complexes, the copper(II) content and the elemental analyses were in agreement with the proposed formulae. Other pseudohalide complexes, $[Cu(N_3)(NCS)(N,N'\text{-diMeen})]_2$ **4** and $[Cu(N_3)(NCO)(N,N\text{-diMeen})]_2$ **5** were obtained for the first time and the yield was 70% in each case. Complex 4 was prepared by the dropwise addition, with stirring, of a solution of NaN_3 (3.00 mmol) and KNCS (3.00 mmol) in 5 cm^3 of water to 25 cm^3 of a methanolic solution containing $Cu(NO_3)_2{\cdot}3H_2O$ (3.00 mmol) and N,N'-diMeen (2.82 mmol). The mixture was stirred for 30 min and the compound formed was filtered, washed with diethyl ether and dried in vacuum. Complex **5** was prepared by a similar procedure. All the preparations were performed at 299 K.

Chemical analysis

Copper content was determined by complexometric titration with standard EDTA solution (0.0100 mol L^{-1}), in the presence of the indicator PAN 0.05 % in ethanol, using a microburet Methrom model E-274 [13]. 'Central Analítica IQ-USP, Brazil' performed elemental analysis of carbon, nitrogen and hydrogen. The results of the analyses are presented in Table 1.

Table 1 Results of chemical analysis of the compounds in %

Compound	Cu		C		N		H	
	found	calc.	found	calc.	found	calc.	found	calc.
$[Cu(N_3)_2(N,N\text{-diEten})]_2$	23.95	24.09	27.21	27.32	42.12	42.48	6.08	6.11
$[Cu(NCO)_2(N,N\text{-diEten})]_2$	24.60	24.09	36.28	36.43	21.11	21.24	6.15	6.11
$[Cu(NCO)_2(N,N\text{-diMeen})]_2$	26.45	26.96	30.34	30.57	23.68	23.77	5.11	5.13
$[Cu(N_3)(NCS)(N,N'\text{-diMeen})]_2$	24.83	25.24	23.74	23.85	33.05	33.38	4.75	4.80
$[Cu(N_3)(NCO)(N,N\text{-diMeen})]_2$	26.38	26.96	25.84	25.47	35.16	35.65	4.95	5.13

Methods

Infrared spectroscopy

The infrared spectra (IR) were recorded on a Nicolet 730 SX-FT spectrometer in the spectral range 4000–200 cm^{-1} with the samples in the form of pellets pressed with cesium iodide.

Thermogravimetric analysis

Thermal analysis (TG/DTG) was carried out under dynamic air atmosphere (20 cm^3 min^{-1}) with a heating rate of 20 K min^{-1}, using a Perkin Elmer TGS-2 thermobalance.

X-ray diffractometry

X-ray powder diffractrograms were obtained with an HGZ 4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height discriminator. The Bragg-Bretano arrangement was adopted using CuK_α radiation (λ=1.54 Å). The peaks were identified using ASTM data files [14].

Results and discussion

The reactions between copper(II) ions and bidentate amines in presence of pseudohalides of alkali metals (Na and K) afforded the compounds **1**–**5**. The complexes were characterized by IR spectroscopy and thermogravimetric analysis. The elemental analysis and thermogravimetric results for the synthesized compounds are in agreement with the proposed formulae.

Infrared spectra

The frequencies (cm^{-1}) of the more significant bands that appear in the spectra of new products are given in Table 2 along with their assignments.

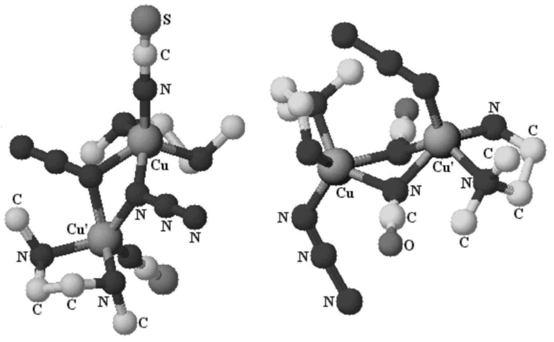
IR spectra and molecular structures determined by X-ray diffraction methods of dimeric compounds **1**–**3** have been already reported and discussed elsewhere [9–11]. Infrared spectra of complexes **4** and **5** show significant shifts of the vibrations related to the diamines when compared with those of the free ligands, supporting their coordination to the copper atom. However, the most important data of these spectra are the spectral regions where vibration modes of the pseudohalide groups are found. The pseudohalide ions N_3^-, NCO^- and NCS^- are versatile ligands, which can coordinate to metallic centers either in a monodentate or bridging fashion [1–3, 15, 16]. As a result, the pseudohalide copper complexes exhibit a remarkable diversity in their structural chemistry. There are an extensive literature dealing with the identification of pseudohalide coordination mode by IR criteria. In general, the pseudohalide stretching vibrations (ν_{as} and ν_s) are the most characteristic ones for transition-metals pseudohalide complexes and allow to clarify the aspects related to the coordination mode of these ions [16–17].

Table 2 IR spectra data (4000–200 cm^{-1}) for compounds [Cu(N_3)(NCS)(N,N'-diMeen)]$_2$ **4** and [Cu(N_3)(NCO)(N,N-diMeen)]$_2$ **5**

Compound	Vibrational frequency/cm^{-1}	Assignment
4	3265 (m), 3206 (m)	νNH
	2930 (w), 2850 (w)	νCH
	2085 (vs)	ν_{as} NCS
	2051 (vs)	ν_{as} N_3
	829 (sh)	ν_s NCS
	652 (vw), 622 (vw), 567 (vw)	δ N_3
	473 (vw)	δ NCS
	394 (m), 349 (m), 305 (m)	ν Cu-N(pseudohalide)
	257 (w), 235 (w)	ν Cu-N(amine)
5	3321 (m), 3260 (vw), 3144 (vw)	ν NH
	2981 (sh), 2930 (w), 2893 (sh)	ν CH
	2227 (vs)	ν_{as} NCO
	2029 (vs)	ν_{as} N_3
	1578 (m)	δ NH
	1346 (m)	ν_s NCO
	1239 (w)	ν_s N_3
	656 (w)	δ NCO
	612 (m)	δ N_3
	501 (w), 419 (sh), 378 (m)	ν Cu-N(pseudohalide)
	279 (m), 257 (w)	ν Cu-N(amine)

m – medium, *s* – strong, *sh* – shoulder, *vs* – very strong, *vw* – very weak, *w* – weak

The $\nu_{as}(N_3)$ and ν_{as}(NCS) modes appear as strong peaks at, respectively, 2051 and 2085 cm^{-1} in IR spectrum of **4**. The shift to higher frequencies of $\nu_{as}(N_3)$ band indicates the end-on bridging mode of azide [18]. This value is very similar to the one observed for **1** (2050 cm^{-1}), the molecular structure of which determined by X-ray crystallography, reveals such bridging fashion for the N_3 group [9]. Concerning the bonding mode of thiocyanate ion, the ν_{as}(NCS) mode is found in the characteristic spectral range of terminal N-bonded thiocyanato [16(a), 19]. The identification of ν_s vibrations is difficult due to their low intensity and the presence of diamine bands in the same region. On the other hand, the $\nu_{as}(N_3)$ band at 2029 cm^{-1}, found in the IR spectrum of **5**, is typical of terminally coordinated azide [9, 18]. In addition, the appearance of $\nu_s(N_3)$ mode as a weak band at 1239 cm^{-1} also indicates the terminal nature of azido group [18]. The end-on bridging mode via nitrogen atom of cyanate ion is supported by the shift to higher frequencies of ν_{as}(NCO) band (2227 cm^{-1}) [16] which is in accordance with those found for the dimers **2** (2210 cm^{-1}) [10] and **3** (2206 cm^{-1}) [11].



4 5

Fig. 1 Proposed structures for the complexes $[Cu(N_3)(NCS)(N,N'\text{-diMeen})]_2$ **4** and $[Cu(N_3)(NCO)(N,N\text{-diMeen})]_2$ **5**, respectively

The strict similarities of $\nu_{as}(N_3)$ mode found for azido-bridged compounds **1** and **4** as well the $\nu_{as}(NCO)$ vibration for cyanato-bridged **2–3** and **5** strongly support a structural analogy among them in the solid state. On the basis of C, H and N microanalysis data, copper contents determination (Table 1) and IR spectroscopy, we suggest centrosymmetric dimeric structures as the preferential forms for the compounds **4** and **5**. Each five-coordinated copper atom is surrounded by five nitrogen atoms; two of them belong to two bridging pseudohalides, one to terminal pseudohalide and two are amine nitrogens. The proposed structures in the solid state for **4** and **5** are illustrated in Fig. 1.

In order to get more information about compounds **1–5** in solid state, we utilized thermogravimetric analysis and the results obtained from this technique are discussed below.

Thermogravimetric analysis

Thermal analysis has become an important technique for studies of metal complexes [20]. In the present paper the application of the thermogravimetric analysis has its main goal in revealing the influence of the pseudohalides and amines on the initial decomposition temperature and on the thermal decomposition mechanisms. Table 3 lists the steps, initial and final temperatures (K), partial and total mass losses (%) for thermal decompositions of **1–5**, in dynamic air atmosphere.

TG and DTG curves for compounds **1** and **2** are shown in Fig. 2 whereas those ones obtained for **3**, **4** and **5** are depicted in Fig. 3. As proved by accordance of X-ray powder diagrams of final products with ASTM-files [14], all compounds decompose giving copper(II) oxide; no other reflection was observed. The analysis of the TG and DTG curves allows to determine the temperature range of mass losses corresponding to degradation stages of complexes **1–5**.

TG-DTG curves show that the thermal decomposition of **1** and **4** occurs in four consecutive steps whereas the decomposition of **2**, **3** and **5** occurs in three consecutive steps. The first mass loss of **1**, in the range 423–443 K, suggests the partial elimination of

Table 3 Thermal analysis data for compounds **1**–**5**

No.	Compound	Step	T_i/K	T_f/K	Δ*m*/%
1	$[Cu(N_3)_2(N,N\text{-diEten})]_2$	1	423	443	27.32
		2	443	503	16.39
		3	503	563	17.76
		4	563	923	13.20
					(74.67)
2	$[Cu(NCO)_2(N,N\text{-diEten})]_2$	1	413	493	33.33
		2	493	703	22.92
		3	703	993	20.45
					(76.77)
3	$[Cu(NCO)_2(N,N\text{-diMeen})]_2$	1	403	553	38.46
		2	553	763	18.59
		3	763	1153	15.96
					(73.01)
4	$[Cu(N_3)(NCS)(N,N'\text{-diMeen})]_2$	1	443	483	35.06
		2	483	503	16.77
		3	503	723	7.62
		4	723	1173	14.85
					(74.30)
5	$[Cu(N_3)(NCO)(N,N\text{-diMeen})]_2$	1	423	503	37.11
		2	503	703	24.02
		3	703	1153	13.05
					(74.18)

T_i=initial temperature; T_f=final temperature; Δ*m*=mass variation
Total percentage mass losses are shown in parentheses for each compound

N,N-diEten. The second and third mass losses, between 443–503 K and 503–563 K, are assigned to the final elimination of the amine and to the partial degradation of azido-groups, respectively. The last mass loss, 563–923 K, corresponds to the complete degradation of azido-groups. The first decomposition step of **2**, observed between 413–493 K, suggests the partial elimination of the N,N-diEten. The second step, in the range 493–703 K, is due to the final elimination of the amine and partial degradation of cyanato-groups. The last step takes place between 703–993 K and corresponds to the complete degradation of cyanato-groups. The first mass loss of **3** occurs between 403–553 K and is assigned to the elimination of two N,N-diMeen molecules. The next mass loss, in the range 553–763 K, indicates the partial degradation of cyanato-groups. The last mass loss, 763–1153 K, corresponds to the final elimination of cyanato-groups. The first decomposition step of **4**, between 443–483 K, suggests the complete elimina-

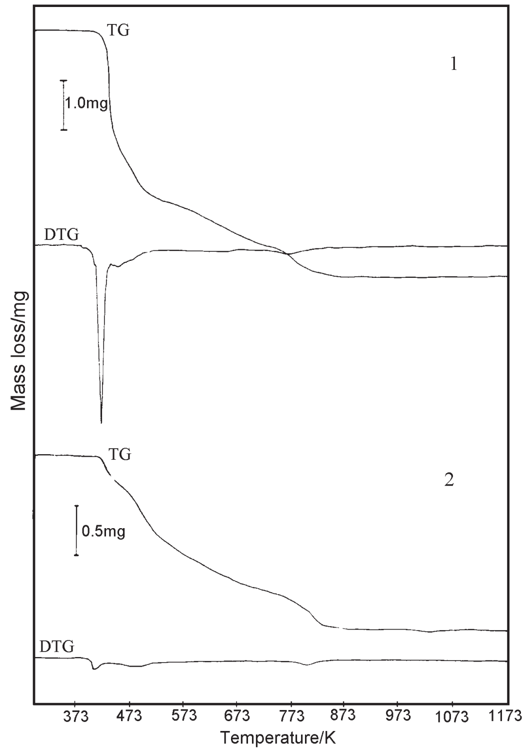


Fig. 2 TG/DTG curves for the complexes $[Cu(N_3)_2(N,N\text{-diEten})]_2$ (**1**) and $[Cu(NCO)_2(N,N\text{-diEten})]_2$ (**2**)

tion of N,N'-diMeen. The second step, in the range 483–503 K, is attributed to the elimination of azido-groups. The third step, 503–723 K, corresponds to the partial degradation of thiocyanato-groups. The last step occurs in the range 723–1173 K and is assigned to the elimination of thiocyanato-groups. At this last step a mass gain has been observed. We attribute it, according to available data [21], to the formation of $CuSO_4$. The formation of copper sulfate is confirmed by its infrared spectrum, that shows absorption bands characteristic of the sulfate group. The copper(II) sulfate then is converted into CuO. Finally, the first mass loss of **5**, observed between 423–503 K, is due to the elimination of N,N-diMeen. The second mass loss, in the range 503–703 K, corresponds to the complete elimination of azido-groups and partial degradation of cyanato groups. The last mass loss, 703–1153 K, is assigned to the final degradation of cyanato groups.

The thermal decomposition steps proposed are supported by the IR spectra of the residues corresponding to the first mass losses of **3**, **4** and **5**, which show no absorption bands corresponding to the vibrational modes of the amines. These data confirm the loss of the amines in the first step of the decompositions of these complexes. A general equation describing the thermal behavior of the complexes is given below.

$$[\mathrm{Cu}(\mu\text{-X})(\mathrm{Y})(\mathrm{L{-}L})]_2+\mathrm{O}_2 \xrightarrow[\text{403–1173 K}]{\substack{\text{I)}-2\mathrm{L{-}L}\\ \text{II)}-2\mathrm{X}^-,-2\mathrm{Y}^-}} 2\mathrm{CuO}$$

X=NNN$^-$, NCO$^-$; Y=NNN$^-$, NCO$^-$, NCS$^-$; L–L=N,N-diEten, N,N-diMeen, N,N'-diMeen

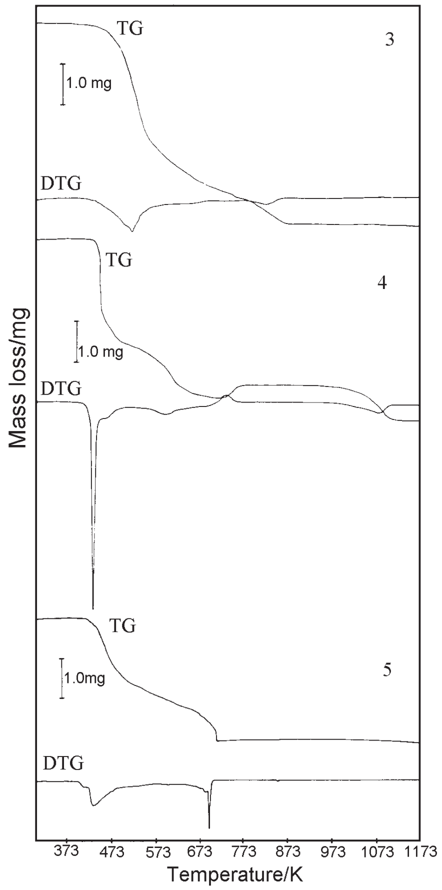


Fig. 3 TG/DTG curves for the complexes [Cu(NCO)$_2$(N,N-diMeen)]$_2$ (**3**), [Cu(N$_3$)(NCS)(N,N'-diMeen)]$_2$ (**4**) and [Cu(N$_3$)(NCO)(N,N-diMeen)]$_2$ (**5**)

Conclusions

The thermal decomposition of the series of copper(II) complexes studied in this work, as well as their stability, depends on the nature of the ligands, as can be inferred from the TG curves. Thus, taking into account the initial temperature of the decomposition process, it was possible to establish the following relative thermal stability order: 3<2<1=5<4.

Furthermore, some conclusions may be drawn from this order. Firstly, the complexes containing mixed pseudohalides have higher stability compared to complexes containing only one pseudohalide. Secondly, the higher thermal stability of azide complex **1** compared to cyanato complex **2**, both containing the same amine, may be explained by a more covalent character of bonding between the azide and the metal center in **1**.

Finally, it is well known that for cyanato complexes **2** and **3** the geometry around the metal and the types of coordination of the pseudohalides are identical. Then, a higher thermal stability of **2** in comparison to **3** may be associated with bond lengths between amino nitrogen atoms and central ion. In the complex 2 with a centrosymmetric structure, the Cu–N bond lengths are 2.102 Å and 1.974 Å [10]; while for **3** the bond lengths are: 2.004, 2.057, 2.003 and 2.085 Å [11]. Thus, the stronger Cu–N bonds present in the complex **2** are in good agreement with the thermal analytical results.

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