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THERMAL CHARACTERIZATION OF MERCURY(II) BIS(DIALKYLDITHIOCARBAMATE) COMPLEXES

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The mercury(II) bis(dialkyldithiocarbamate) complexes, $Hg(S_2CN\text{-}R_2)_2$, in which *R*=ethyl, *n*-propyl, *n*-butyl and *iso*-butyl were characterized by TG, DSC, FTIR and elemental analysis. The TG curves presented two thermal decomposition stages; the first stage can be attributed to the partial decomposition of ligand and also to mercury sulfide decomposition. The second stage is representative for the decomposition of ligand fragments. The overlaid TG/DSC curves indicated that the decomposition of the complexes takes place the liquid phase. According to the isothermal kinetic data the phase-boundary controlled kinetic models describes the best the decomposition of complexes. The data obtained by the Ozawa method suggest the following stability order for the complexes: *i*Bu>*n*Pr>*n*Bu>Et.

Keywords: *mercury, Ozawa method, thermal decomposition*

Introduction

The interest in the chemistry of dithiocarbamate consists not only the analytical applications of these compounds, but also in their wide industrial utilization, for instance, in the field of pesticides and vulcanization. The thermochemistry of metal dithiocarbamates has been widely studied but little is known about their thermal decomposition kinetics [1–5].

Thermoanalytical methods have a great interest in the R&D community, due to their wide applicability in academic researches and mainly in the industrial processes that involving the thermal decomposition reactions of solids [6–10].

The thermal decomposition reactions have been studied by non-isothermal and isothermal thermogravimetry. The non-isothermal method proposed by Ozawa determines the value of the activation energy, and also the pre-exponential factor, by means of several thermogravimetric curves obtained at different heating rates [11]. In the present work, such method was used to obtain the aforementioned kinetic parameters by employing the following equation:

$$\log\phi = \log\left[\frac{AE}{Rg(\alpha)}\right] - 2.315 - 0.4567\frac{E}{RT} \qquad (1)$$

where α=decomposed fraction; T=temperature; ϕ=heating rate; E=activation energy; R=ideal gas constant; A=pre-exponential factor.

The aim of this work is to study the thermal and kinetic behavior of the mercury(II) bis(dialkyldithiocarbamate) complexes, $Hg(S_2CN\text{-}R_2)_2$, in which *R*=ethyl (Et), *n*-propyl (*n*Pr), *n*-butyl (*n*Bu) and *iso*-butyl (*i*Bu) by thermal techniques, using non-isothermal and isothermal methods.

Experimental

The mercury(II) bis(dialkyldithiocarbamate) complexes were synthesized by the direct reaction between mercury chloride, the appropriate secondary amine and carbon disulfide. The synthesis was carried out in an ice bath. The formed crystalline yellow precipitate was filtered and recrystallized [12, 13].

Instrumental background

The melting temperatures of all complexes were determined using a model MQAPF-301 Microquímica apparatus.

The analyses of carbon, hydrogen and nitrogen were obtained in a model PE-240 Perkin Elmer Elemental Analyzer.

The infrared spectra were recorded in the 4000–400 cm^{-1} range using a model MB-102 Bomem apparatus and KBr pellets.

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The TG curves were obtained with a Shimadzu TGA-50 Thermobalance, under nitrogen atmosphere (flow rate: 50 mL min^{-1}) and different heating rates as 5, 10 and 15 K min^{-1}, were used in the 28–500ºC temperature range. The initial sample masses were 3.0±0.1 mg.

The calorimetric curves were obtained with a Shimadzu DSC-50 Differential Scanning Calorimeter, at a heating rate of 10 K min^{-1}, using the same conditions as it was written above for TG measurements.

Results and discussion

The melting temperatures of the complexes, obtained by a conventional equipment (analogic) and by DSC method are in a good agreement as it can be seen in Table 1.

Table 1 Melting temperatures of the complexes

Complexes	MQAPF-301 temperature/ºC	DSC temperature/ºC
$\mathrm{Hg(S_2CN\text{-}Et_2)_2}$	142.4	142.4
$\mathrm{Hg(S_2CN\text{-}}n\mathrm{Pr_2)_2}$	108.2	104.9
$\mathrm{Hg(S_2CN\text{-}}i\mathrm{Bu_2)_2}$	95.8	94.9
$\mathrm{Hg(S_2CN\text{-}}n\mathrm{Bu_2)_2}$	79.7	78.9

Elemental analysis

Table 2 presents the calculated and experimental values for the analysis of carbon, hydrogen and nitrogen of the synthesized compounds.

These results show that the experimentally obtained values agree with the stoichiometry of the complexes, indicating that the complexes were successfully synthesized.

Table 2 Results of the elemental analysis of the complexes

Complexes	Calculated/%			Experimental/%		
	C	H	N	C	H	N
$\mathrm{Hg(S_2CN\text{-}Et_2)_2}$	35.47	5.97	4.60	35.30	5.40	4.70
$\mathrm{Hg(S_2CN\text{-}}n\mathrm{Pr_2)_2}$	30.40	5.10	5.10	30.60	4.90	4.90
$\mathrm{Hg(S_2CN\text{-}}i\mathrm{Bu_2)_2}$	35.47	5.97	4.60	35.30	5.40	4.70
$\mathrm{Hg(S_2CN\text{-}}n\mathrm{Bu_2)_2}$	35.47	5.97	4.60	35.40	5.50	4.50

Infrared spectroscopy

The infrared absorption spectra of the complexes presented a strong band in the 2910 and 2970 cm^{-1} region, corresponding to the νC–H vibration frequency. Furthermore, a strong band appeared between 1450 and 1590 cm^{-1}, evidencing the existence of a $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond. A medium band at 950 and 1000 cm^{-1} were attributed to νC–S, which confirm the bidentate character of ligand proposed by Bonati and Ugo [14]. The main absorption bands of the complexes are listed in Table 3.

Thermoanalytical study

The TG curves presented similar characteristics for all the studied complexes (Table 4). The higher heating rates, applied the same sample mass, increased the initial decomposition temperature.

The non-isothermal TG curves presented two mass loss stages. The first one can be attributed to the partial decomposition of ligand and the mercury sulfide. The second stage is representative to the decomposition of the fragments of ligands.

The DSC curves presented a sharp endothermic peak between 78 and 142°C for all the complexes, which can be attributed to their melting. These values are very close to the results obtained by conventional melting point determination. Another important transition, corresponding to the ligand decomposition, was observed between 244 and 304ºC, resulting a wide endotherm peak. An exception is the case of $\mathrm{Hg(S_2CN\text{-}Et_2)_2}$, which presents an exothermic transition.

Table 5 presents the transition temperatures attributed to the melting and to the decomposition of the complexes and their respective enthalpies.

By the comparison of the TG and DSC curves it can be stated that the decomposition of complexes takes place in the liquid phase. In this aspect the control of sample particle size is not very important. Figure 1 shows the TG and DSC curves of $\mathrm{Hg(S_2CN\text{-}}n\mathrm{Pr_2)_2}$ complex, the heating rate was 10ºC min^{-1}.

Table 3 Main absorption bands observed in the infrared spectra

Complexes	Stretching/cm^{-1}			
	C–H	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	$\overset{\cdots}{-}\mathrm{C{-}S}$	$\mathrm{C}\overset{\cdots}{-}\mathrm{S}$
$\mathrm{Hg(S_2CN\text{-}Et_2)_2}$	2918.86(s)	1496.34(s)	1071.86(m)	984.83(m)
$\mathrm{Hg(S_2CN\text{-}}n\mathrm{Pr_2)_2}$	2962.48(s)	1492.09(s)	1087.42(m)	965.27(m)
$\mathrm{Hg(S_2CN\text{-}}i\mathrm{Bu_2)_2}$	2958.87(s)	1489.96(s)	1088.69(m)	978.49(m)
$\mathrm{Hg(S_2CN\text{-}}n\mathrm{Bu_2)_2}$	2959.10(s)	1491.82(s)	1092.24(m)	951.37(m)

Intensity: s – strong; m – medium

Table 4 TG data (heating rate: 10 K min^{-1})

Complexes	Stage	Temperature range/°C	Mass loss/%
$Hg(S_2CN\text{-}Et_2)_2$	1st	237.80–325.96	79.80
	2nd	326.82–395.35	15.86
	residue	*>395.35*	*4.34*
$Hg(S_2CN\text{-}nPr_2)_2$	1st	243.48–336.08	87.81
	2nd	336.90–388.77	8.70
	residue	*>388.77*	*3.49*
$Hg(S_2CN\text{-}iBu_2)_2$	1st	225.15–339.45	91.40
	2nd	340.28–370.37	6.01
	residue	*>370.37*	*2.59*
$Hg(S_2CN\text{-}nBu_2)_2$	1st	243.36–328.51	90.26
	2nd	329.37–416.23	6.05
	residue	*>416.23*	*3.69*

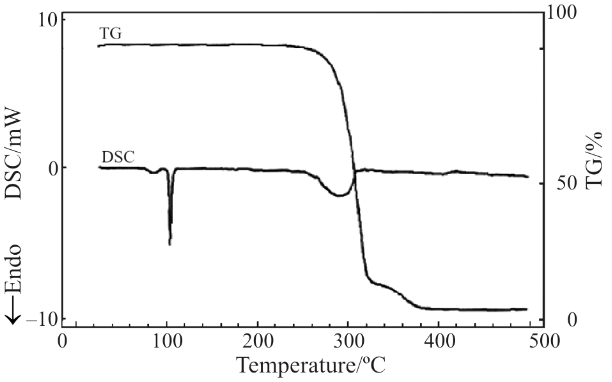

Fig. 1 TG and DSC curves of $Hg(S_2CN\text{-}nPr_2)_2$ complex

Kinetic analysis of complexes

The kinetic models of decomposition reactions of complexes and their rate constants (*k*) were determined by the isothermal method. The selection between the different models of heterogeneous reactions based on the experimental data. The best fitting corresponds to the best linear regression coefficient.

For $Hg(S_2CN\text{-}Et_2)_2$ and $Hg(S_2CN\text{-}nPr_2)_2$ complexes the kinetic model that best fitted the experimental curves was the 2-dimensional phase-boundary controlled model (R2). On the other hand, for the $Hg(S_2CN\text{-}iBu_2)_2$ and $Hg(S_2CN\text{-}nBu_2)_2$ complexes the best fit corresponds to the one-dimensional phase-boundary controlled model (R1). The values of the rate constants are coherent with their expected temperature dependence (Table 6).

Table 5 Temperatures and enthalpies of main transitions, obtained by DSC

Complexes	Melting temperature/°C	ΔH_{fus}/J g^{-1}	Decomposition temperature/°C	ΔH_{dec}/J g^{-1}
$Hg(S_2CN\text{-}Et_2)_2$	142.38	42.17	244.99	161.85
$Hg(S_2CN\text{-}nPr_2)_2$	104.97	44.65	304.41	217.46
$Hg(S_2CN\text{-}iBu_2)_2$	94.99	42.21	304.37	201.03
$Hg(S_2CN\text{-}nBu_2)_2$	78.91	43.22	301.91	305.34

Table 6 Rate constants of $Hg(S_2CNR_2)_2$ complexes

Parameters	Complexes				
	$Hg(S_2CN\text{-}Et_2)_2$ – Isothermal temperature/°C				
	276	279	282	285	288
k/s^{-1}	7.26E-04	8.28E-04	9.64E-04	1.08E-03	1.23E-03
r	0.9987	0.9982	0.9988	0.9991	0.9988
	$Hg(S_2CN\text{-}nPr_2)_2$ – Isothermal temperature/°C				
	276	279	282	285	288
k/s^{-1}	3.46E-04	4.13E-04	5.62E-04	5.97E-04	7.19E-04
r	0.9992	0.9976	0.9999	0.9990	0.9993
	$Hg(S_2CN\text{-}iBu_2)_2$ – Isothermal temperature/°C				
	261	264	267	270	273
k/s^{-1}	1.84E-04	2.11E-04	2.43E-04	2.93E-04	3.52E-04
r	0.9992	0.9988	0.9989	0.9985	0.9973
	$Hg(S_2CN\text{-}nBu_2)_2$ – Isothermal temperature/°C				
	242	248	254	257	260
k/s^{-1}	6.24E-05	8.92E-05	1.23E-04	1.38E-04	1.83E-04
r	0.9998	0.9998	0.9995	0.9988	0.9995

The kinetic parameters (activation energy and pre-exponential factor) were determined by the non-isothermal Ozawa method [11] using the TG curves recorded with 5, 10 and 15 K min^{-1} heating rates and temperature range related to the decomposition of complexes (Table 7).

Table 7 Kinetic parameters obtained by Ozawa method

Complexes	E/kJ mol^{-1}	A/s^{-1}
$Hg(S_2CN\text{-}Et_2)_2$	149.13	8.40E-14
$Hg(S_2CN\text{-}n\text{Pr}_2)_2$	170.94	5.11E-16
$Hg(S_2CN\text{-}i\text{Bu}_2)_2$	178.53	1.99E-17
$Hg(S_2CN\text{-}n\text{Bu}_2)_2$	150.72	9.18E-14

The results obtained upon the utilization of the Ozawa method suggest the following stability order of complexes:

*i*Bu>*n*Pr>*n*Bu>Et

This stability order can be attributed, probably, due to the inductive effect of the alkyl substituents.

Conclusions

The infrared spectroscopy investigation of complexes was verified that the dialkyldithiocarbamate ligands are bidentate. The TG profiles for all the complexes presented two thermal decomposition stages, the first stage can be attributed to the partial decomposition of ligand and to the mercury sulfide decomposition. The second stage can be attributed to the decomposition of ligand fragments. The comparison of the TG and DSC curves showed that the thermal decomposition of complexes occurs in liquid phase.

The isothermal kinetic data indicated that the thermal decomposition reactions of the complexes were best described by the one-dimensional (R1) and two-dimensional phase-boundary controlled model (R2).The activation energy data obtained by the Ozawa method suggest the *i*Bu>*n*Pr>*n*Bu>Et stability order for the complexes.

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