A THERMAL ANALYSIS STUDY OF DITHIZONE AND DITHIZONATES OF MERCURY, SILVER AND BISMUTH

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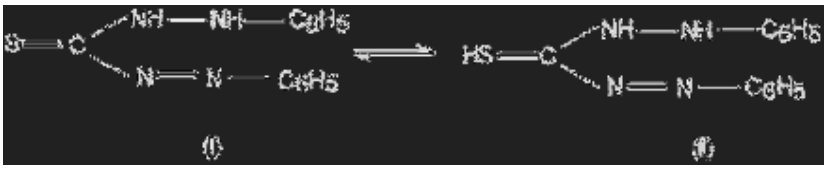
ABSTRACT: Solid dithizonates of Hg(I), Ag(I) and Bi(III) have been prepared. Thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), X ray diffraction powder patterns and elemental analysis have been used to characterize and to study the thermal stability and thermal decomposition of the dithizone and of these dithizonates.
KEYWORDS: dithizone, dithizonates, mercury, silver, bismuth, thermal decomposition.

Introduction

In organic solvents dithizone exists in the keto (I) and the enol (II) tautomeric forms.



Studies of solid state dithizonates have been carried out on the crystal structure of some transition metal by X-ray diffraction[2,5,6,7], and the infrared spectra of a number of metal dithizonates[4]. Preparation and thermal analysis study of some transition metal dithizonates have also been reported[3,8]. No reference has been found to the application of TG and DSC in the study of mercury and bismuth dithizonates.

In this work, Hg(I), Ag(I) and Bi(III) dithizonates were prepared and investigated by complexometry, elemental analysis, TG, DTG, DSC and X-ray diffraction powder patterns.

Experimental

Aqueous solutions of the metal ions were prepared by dissolving the respective nitrate. The solid state complexe of mercury was prepared by mixing solution of 0.05% (w/v) in ketone, to effect total precipitation of mercury dithizonate, as described previously[3]. The silver and bismuth dithizonates, due to decomposition (Ag) and

hydrolysis (Bi) during the washing of the precipitates, these compounds were prepared by solvent extraction. Thus reaction of aqueous solutions of metal ions with a dithizone solution of 0.05% (w/v) in chloroform was effected in a separation funnel. After to shake vigorously, the organic phase containing the respective dithizonates were separated and the chloroform evaporated. The compounds were stored in a desiccator over anhydrous calcium chloride.

The silver and bismuth contents of the complexes were determined by complexometric titration with standard EDTA solution[1], after samples have been heated in a digestion apparatus with concentrated nitric acid and 30% hydrogen peroxide added dropwise. The metal contents were also determined from TG curves. The dithizonate contents of these compounds were determined from the TG curves and confirmed by carbon, nitrogen, sulphur and hydrogen micro-analytical determinations.

For the mercury dithizonate, the metal content was determined by cold vapour atomic absorption spectroscopy (CVAAS) and the ligand content was determined by Nessler Method (colorimetric determination of nitrogen).

The TG and DTG curves were recorded on a Perkin Elmer TGS-2, thermogravimetric system with an air flow of 5 mL min^{-1}, a heating rate of 20°C min^{-1} and a platinum crucible. The DSC curves were obtained using a Mettler TA 4000 thermal analysis system with an air flow rate of 150 mL min^{-1}, and a heating rate of 20°C min^{-1}, and aluminium crucible with perforated cover.

X-ray powder patterns were obtained with an HGZ 4/B horizontal diffractometer (GDR) equipped with a proportional counter and pulse height discriminator. The Bragg-Brentano arrangement was adopted using CoKα (λ = 1.78897**Å**) and a setting of 38 kV and 20 mA.

Carbon, nitrogen, sulphur and hydrogen were determined by microanalytical procedures using CE Intruments, EA 1110 CHNS-) apparatus.

Results and discussion

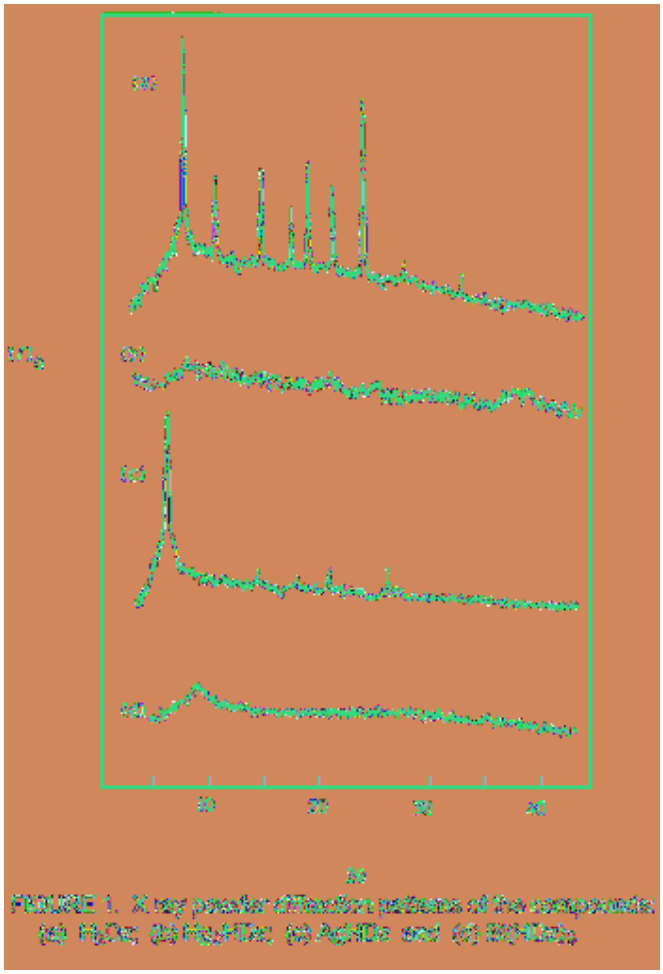
Table 1 presents the analytical and thermoanalytical (TG) data and Table 2 the elemental analysis results, from which the formula AgHDz and $Bi(HDz)_3$ can been established, where HDz is the dithizonate present in the keto form. For the mercury complexe due to total volatilization up to 630°C, no thermoanalytical data were possible to obtain, and incompatible results were also observed in the elemental analysis data. Thus, the formula Hg_2HDz was established through analytical data obtained by CVAAS and Nessler Method. All complexes were obtained in the anhydrous form.

TABLE 1 - Analytical and thermoanalytical (TG) results

Compounds	Metal (%)				HDz* (L_{eq} %)		Nitrogen (%)	
	Theor	TG	EDTA	AAS	Theor	TG	Theor	Nessler
AgHDz	32.70	32.49	32.91	-	68.30	64.38	-	-
$Bi(HDz)_3$	21.64	21.37	21.37	-	46.49	45.82	-	-
Hg_2HDz	61.11	-	-	58.62	-	-	6.66	6.36

*HDz = dithizonate

The X ray powder patterns, Fig. 1, show that the dithizone and the silver complexe have a crystalline structure, while the mercury and bismuth complexes indicate an amorphous structure.



The TG and DSC curves of the dithizone and dithizonates are shown in Fig. 2. For the dithizone, these curves, Fig. 2(a), show thermal stability up to 100°C and that the thermal decomposition occurs in three consecutive steps between 100°C and 600°C. The first step observed up to 130°C, the mass loss occurs through a very fast process due to combustion (explosion) with loss of 35.7%. The second and third steps up to 250°C and 600°C, the mass losses correspond to 25.6% and 38.7% respectively without formation of carbonaceous residue.

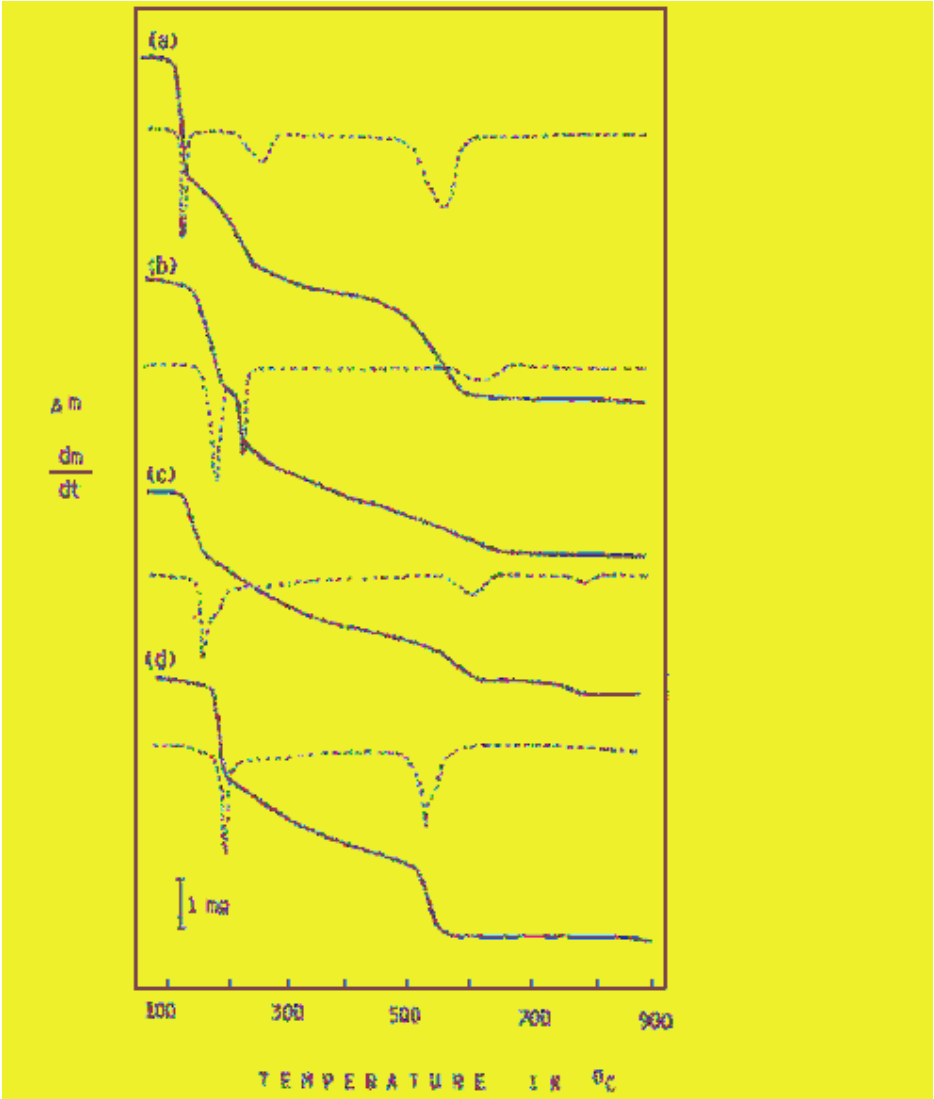


FIGURE 2. TG and DTG curves of the compounds: (a) H_2Dz(6.330 mg); (b) Hg_2HDz(4.980 mg); (c) $AgHDz$(5.540 mg) and (d) $Bi(HDz)_3$(6.480 mg)

The thermal decomposition of mercury (I), silver (I) and bismuth (III) complexes, show mass losses in steps which depend on the metal present, and it is characteristic for each complexe.

For the mercury(I) complexe, the TG and DTG curves, Fig. 2(b), show mass losses in three consecutive steps between 130°C and 690°C. The first and second steps up to 200°C and 230°C, respectively, the thermal decomposition occurs through a fast and very fast process due to combustion (explosion), with losses of 40.6% and 20.3%. The third step, between 230°C and 690°C, the mass loss occurs slowly and correspond to 39.1% with total loss of the complexe.

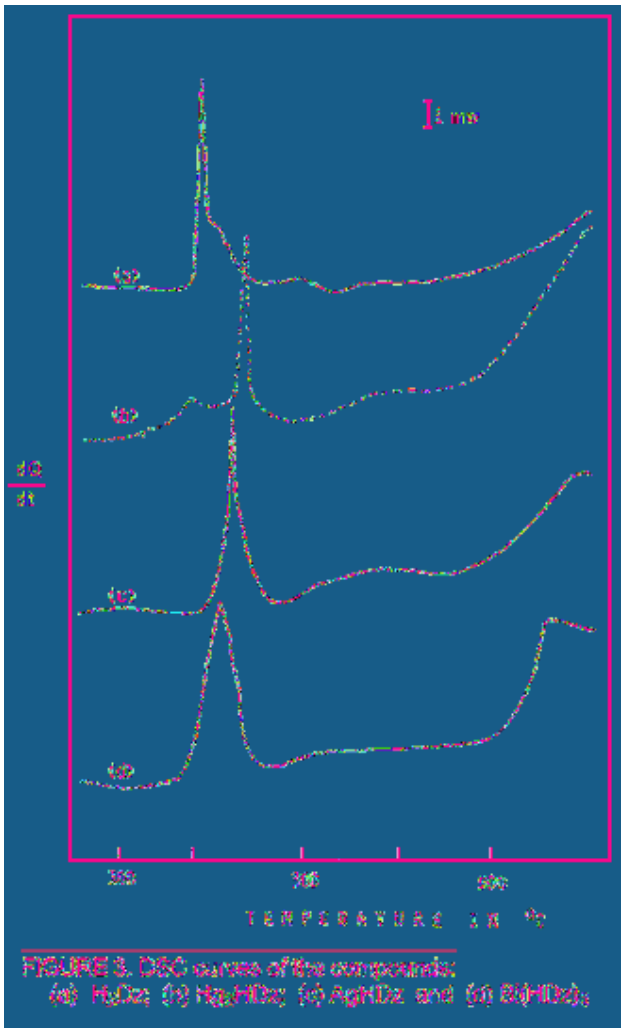
For the silver complexe, the TG and DTG curves, Fig. 2(c), show mass losses in three consecutive steps between 120°C and 790°C. The first step observed up to 180°C, that occurs through a fast process is due to combustion

(explosion) of the sample, with loss of 21.7%. The second step observed between 180°C and 640°C, with loss of 39.2% gives rise to a mixture of silver sulphide and sulphate in no simple stoichiometry relation. The presence of sulphide and sulphate in the residue were confirmed by qualitative tests on residue as indicated by the TG and DTG curves. These result are in agreement with the studies of Pariaud and Archinard[8]. The third step observed between 750°C and 800°C, with loss of 4.1% is ascribed to the thermal decomposition of the mixture of silver sulphide and sulphate to the silver oxide. The formation of silver oxide as final residue is in disagreement with the literature data[8], and it is probably due to the experimental conditions that were not the same.

In the bismuth dithizonate, the TG and DTG curves, Fig. 2(d), show mass losses in two consecutive steps between 170°C and 580°C. The first mass loss up to 210°C, that occurs through a very fast process is due to combustion (explosion) of the sample with loss of 29.7%. The second step observed up to 580°C, with loss of 45.9% is ascribed to the final thermal decomposition of the complexe with formation of bismuth oxide, Bi_2O_3, as residue.

In previous experiments, when samples of 10 mg of the compounds were heated at a rate of 20°C min^{-1} in a furnace in a platinum crucible, explosion with projection of materials were observed for all compounds, where the TG curves show a very fast mass losses in the the first step.

The DSC curves are shown in fig. 3. These curves show exothermic peaks and exotherm up to 600°C, all of which are in accord with the mass losses observed in the TG and DTG curves.



For the dithizone and dithizonates of mercury, silver and bismuth, Fig. 3 (a-d), the sharp exothermic peaks at 181°C, 232°C, 220°C and 208°C respectively are attributed to combustion and are in agreement with the TG and DTG data. The small exothermic peak at 173°C observed only for the mercury complexe, is ascribed to the crystallization process that precedes the combustion. The exotherm observed in all the curves after the combustion is attributed to the final oxidation of the residue resulting from the combustion process.

Conclusion

The X-ray powder patterns verified that the ligand and the Ag(I) complexe have a crystalline structure, and for the Hg(I) and Bi(III) complexes indicate and amorphons structure.

The TG, DTG and DSC curves provided previously unreported information about the thermal stability and thermal decomposition of Hg(I) and Bi(III) dithizonates.

Aknowledgements

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RESUMO: *Foram preparados os ditizonatos de Hg (I), Ag (I) e Bi (III). Termogravimetria (TG), termogravimetria derivada (DTG), calorimetria exploratória diferencial (DSC), difratometria de raios X pelo método do pó e análise elementar foram usados para caracterizar e para estudar a estabilidade térmica e a decomposição térmica da ditizona e destes ditizonatos.*
PALAVRAS-CHAVE: *ditizona, ditizonato, mercúrio, prata, bismuto, decomposição térmica.*

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