Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 405 (2003) 219–224

thermochimica acta

www.elsevier.com/locate/tca

Synthesis, characterization and thermogravimetric study of zinc group halides adducts with imidazole

Maria de F.V. de Moura[a], Ótom A. de Oliveira[a], Robson F. de Farias[b,*]

[a] Departamento de Química, Universidade Federal do Rio Grande do Norte, CP 1662, 59078-970 Natal, Rio Grande do Norte, Brazil
[b] Departamento de Química, Universidade Federal de Roraima, CP 167, 69301-970 Boa Vista, Roraima, Brazil

Received 29 October 2002; received in revised form 12 February 2003; accepted 17 March 2003

Abstract

The synthesis, characterization and thermogravimetric study of the adducts $ZnCl_2·2Imi$, $ZnBr_2·2Imi$, $CdCl_2·Imi$, $CdCl_2·2Imi$, $CdBr_2·2Imi$, $CdBr_2·3Imi$, $CdI_2·2.5Imi$, $HgCl_2·2Imi$, $HgBr_2·1.5Imi$ and $HgI_2·1.5Imi$ (Imi = imidazole) is reported. The following sequence of thermal stability is observed for the synthesized adducts: $Zn > Hg > Cd$. It is also verified that larger cations, as well as larger anions, result in a smaller number of imidazole molecules in the coordination sphere of the considered cation and that hard acids exhibit stronger bonds to imidazole than soft acids, and this fact is reflected in the thermal stability sequence. $ZnCl_2·2Imi$ behaves as a non-electrolyte in acetonitrile and ethanol, whereas $ZnBr_2·2Imi$ is a non-electrolyte in acetonitrile and a 1:1 electrolyte in ethanol. $CdI_2·2.5Imi$ is a non-electrolyte in acetonitrile and a 1:2 electrolyte in ethanol.

Keywords: Imidazole; Adducts; Zinc group halides; Thermogravimetry

1. Introduction

Thermochemical techniques such as thermogravimetry, differential scanning calorimetry and solution calorimetry have been recently employed to the study of a series of coordination compounds of Zn(II), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Sn (II) and Ce(IV) with molecules of biological interest, such as amino acids, or model molecules related with molecules of biological interest, such as ethyleneurea, ethylenethiourea and propyleneurea [1–13].

Imidazole is a very important model molecule since the imidazole ring occurs in a series of biological molecules such as in histidine, in Vitamin B_{12} and biotin as well as many chemotherapic agents [14].

The aim of this publication is to report the synthesis, characterization and thermogravimetric study of the adducts $ZnCl_2·2Imi$, $ZnBr_2·2Imi$, $CdCl_2·Imi$, $CdCl_2·2Imi$, $CdBr_2·2Imi$, $CdBr_2·3Imi$, $CdI_2·2.5Imi$, $HgCl_2·2Imi$, $HgBr_2·1.5Imi$ and $HgI_2·1.5Imi$ (Imi = imidazole). As will be shown, the study of such compounds has provided some interesting insights into the coordination features of imidazole molecules to transition metal cations.

2. Experimental

All reagents used were of analytical grade and were employed without further purification.

---

* Corresponding author. Present address: Instituto de Química, Unicamp, Universidade Estadual de Campinas, CP 6154, 13083-970 Campinas, SP, Brazil. Fax: +55-19-3788-3109.
E-mail address: robsonfarias@aol.com (R.F. de Farias).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00191-6

2.1. Synthesis

2.1.1. $ZnCl_2 \cdot 2Imi$

Stoichiometric amounts of zinc chloride (previously dried at 383 K for 5 days) and imidazole were mixed in a glass ampoule which was then sealed. The sealed ampoule was then placed in an oil bath at 403 K for 36 h. This direct synthesis was chosen because no solvent was found, in which the adducts were soluble and the product would precipitate.

2.1.2. $ZnBr_2 \cdot 2Imi$

Stoichiometric amounts of zinc bromide and imidazole were dissolved in acetone and the resulting solutions mixed. The obtained with precipitate was then filtered off, exhaustively dried with acetone, and then dried under vacuum at ambient temperature for 72 h.

2.1.3. $CdCl_2 \cdot Imi$, $CdCl_2 \cdot 2Imi$, $CdBr_2 \cdot 2Imi$, $CdBr_2 \cdot 3Imi$ and $CdI_2 \cdot 2.5Imi$

These compounds were prepared similar to $ZnBr_2 \cdot 2Imi$, but using ethanol as solvent. The metal halide–imidazole stoichiometric ratios employed in these cases were 1:1, 1:2, 1:2, 1:4 and 1:4, respectively. Thus, it is verified that for cadmium bromide and cadmium iodide, the maximum number of imidazole molecules per each cadmium cation to produce a stable (from a thermodynamic point of view) compound is 3 and 2.5, respectively, at least for compounds prepared at ambient temperature and pressure.

For the cadmium iodide adduct, the formation of a precipitate was not observed, and the crystalline product was obtained after evaporation of the solvent.

2.1.4. $HgCl_2 \cdot 2Imi$, $HgBr_2 \cdot 1.5Imi$ and $HgI_2 \cdot 1.5Imi$

$HgCl_2 \cdot 2Imi$ and $HgBr_2 \cdot 1.5Imi$ compounds were prepared as $ZnBr_2 \cdot 2Imi$, but using ethanol as solvent. The mercury iodide compound was prepared by mixing in a 1:2 ratio anhydrous mercury iodide and imidazole. The obtained mixture looked oily and was soluble in a series of solvents as ethanol, acetone, ethyl ether and carbon tetrachloride. In water, the “oil” produced a white precipitate which was washed with deionized water and dried under vacuum at room temperature for 1 week.

The mercury halide:imidazole stoichiometric ratios employed were 1:2, 1:4 and 1:2 for the chloride, bromide and iodide adducts, respectively. Thus, it was verified that for mercury bromide and mercury iodide, the maximum number of imidazole molecules per cadmium cation to produce a stable (from a thermodynamic point of view) compound is 1.5, at least for compounds prepared at room temperature and pressure.

2.2. Characterizations

Carbon, hydrogen and nitrogen elemental analysis was performed in a Perkin-Elmer microanalyzer, model 2400. The metal and halide quantitative determinations were performed by volumetric titration with EDTA and potentiometric titration with silver nitrate aqueous solution, respectively.

The infrared spectra were obtained on a Perkin-Elmer 1750 spectrophotometer, by using KBr discs or CsI windows. The thermogravimetric curves were obtained in a TGA-7 Perkin-Elmer apparatus under nitrogen atmosphere with a flow rate of $100\,cm^3\,min^{-1}$ and a heating rate of $10\,K\,min^{-1}$.

Conductance measurements were performed at 302 K, for $ZnCl_2 \cdot 2Imi$, $ZnBr_2 \cdot 2Imi$, and $CdI_2 \cdot 2.5Imi$ by using a Metrohm Herisau apparatus model E518. Ethanol and acetonitrile were employed as solvents. Conductance measurements were not performed for the other compounds due to the fact that they are not soluble in the solvents used. Acetonitrile and ethanol are two good solvents for conductance measurements due to their high dielectric constant, low viscosity and low coordination capacity [15].

3. Results and discussion

The elemental analysis results obtained are in agreement with the proposed formulae. Based on the calculated formulae for cadmium and mercury halide compounds it is possible to say that larger cations (mercury), as well as larger anions (iodide) result in a smaller number of imidazole molecules in the coordination sphere of the considered cation, at least for compounds prepared at room temperature and pressure. Furthermore, a non-integer number of imidazole molecules is observed for cadmium iodide and mercury bromide and iodide compounds, suggesting that these compounds associate, with the imidazole

Table 1
Main infrared bands (cm^{-1}) for imidazole adducts with zinc group halides

Compound	ν_a(NH)	ν_s(NH)	δ_a(HN–)	δ_s(HN–)	ρ_r(HN–)
Imidazole	3330	3124	1542	1098	620
$ZnCl_2\cdot$2Imi	3310	3122	1522	1072	646
$ZnBr_2\cdot$2Imi	3336	3128	1540	1098	648
$CdCl_2\cdot$Imi	3342/3236	3138	1536	1092	610
$CdCl_2\cdot$2Imi	3340/3236	3138	1538	1092	610
$CdBr_2\cdot$2Imi	3264	3130	1532	1096	606
$CdBr_2\cdot$3Imi	3260	–	–	–	–
$CdI_2\cdot$2·5Imi	3296	3126	1530	1094	600
$HgCl_2\cdot$2Imi	3216	3138	1546	1086	638
$HgBr_2\cdot$1.5Imi	3214	3132	1544	1082	634
$HgI_2\cdot$1.5Imi	3342	318	1534	1082	644

molecule forming bridges between different metal cations. Such facts have obvious possible implications from a biological point of view.

The main infrared bands are summarized in Table 1. From these data, a coordination though nitrogen can be inferred.

By comparison of the obtained thermogravimetric curves the following general thermal stability sequence could be pointed out: Zn > Hg > Cd. For zinc compounds Br > I, for cadmium compounds Cl > I > Br and for mercury compounds Cl = Br > I. As thermal stability criterion was used the onset temperature for the ligand loss process. The mass loss steps observed for all compounds are summarized in Table 3. For cadmium adducts, the last mass loss step is in each case due to the sublimation of the cadmium halide. As an illustrative example, the TG and DTG curves for $CdBr_2\cdot$3Imi are shown in Fig. 1. For such a compound, the thermal degradation sequence is as follows:

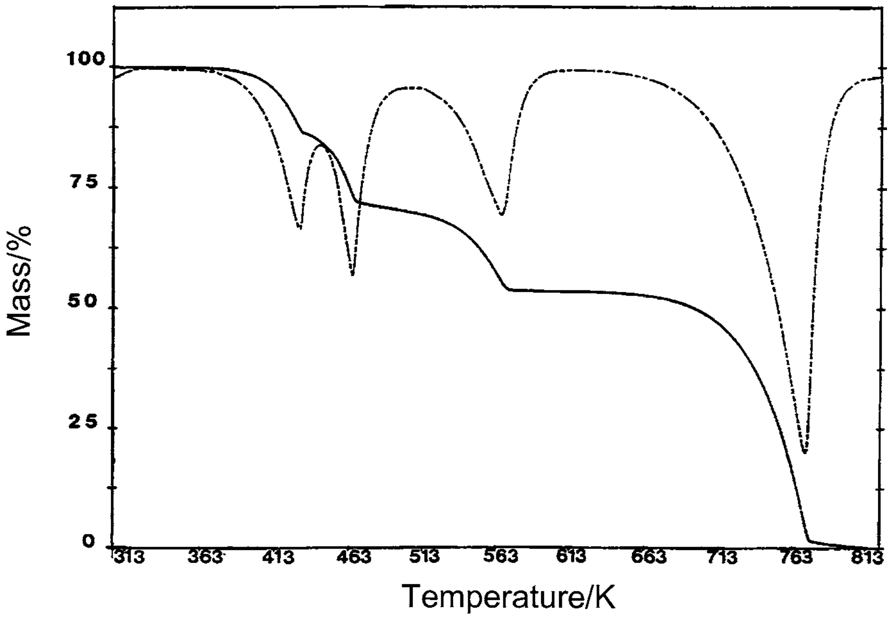

Fig. 1. Thermogravimetric (—) and derivative (–···–) curves for $CdBr_2\cdot$3Imi.

(a) $CdBr_2 \cdot 3Imi\ (s) \rightarrow CdBr_2 \cdot 2Imi\ (s) + Imi\ (g)$,
(b) $CdBr_2 \cdot 2Imi\ (s) \rightarrow CdBr_2 \cdot Imi\ (s) + Imi\ (g)$,
(c) $CdBr_2 \cdot Imi\ (s) \rightarrow CdBr_2\ (s) + Imi\ (g)$,
(d) $CdBr_2 \cdot (s) \rightarrow CdBr_2\ (g)$.

Similar thermal decomposition sequences could be proposed for all compounds studied. For all compounds, the experimental values of the ligand mass loss steps are in good agreement (±5%) with the calculated values, taking into account the elemental analysis formulae.

As can be verified from Table 2, for cadmium chloride the monoadduct is more stable than the bisadduct. Such fact can be understood considering either an ionic or a covalent view of the metal–imidazole bond formation. From an ionic point of view, in the monoadduct, the positive charge of the cation is attracting only one electron pair of the ligand molecule, whereas in the bisadducts there are two electron pairs being attracted, resulting in weaker bonds. From a covalent point of view, it may be supposed that in the monoadduct, the overlapping of metal and ligand frontier orbitals is most effective, resulting in stronger bonds. Based on the observed thermal stability sequence could also be supposed that harder acids (zinc) produce stronger bonds with imidazole (whose coordination site is nitrogen, a hard base) than soft (mercury) acids. Since only the cadmium iodide adduct exhibits a single mass loss step due to the release of imidazole molecules, it can be supposed that for the other compounds the imidazole molecules are not located at equivalent (from a energetic point of view) coordination sites.

For mercury chloride and bromide adducts, two mass loss steps are observed, with the first one due to the release of imidazole molecules. With the mercury iodide adduct, only a single mass loss is observed, possibly a superimposition of imidazole molecules release and sublimation of mercury halide. As an illustrative example, the TG and DTG curves for $HgCl_2 \cdot 2Imi$ are shown in Fig. 2.

For zinc halide adducts a single mass loss step due to the release of imidazole molecules is observed suggesting that both ligand molecules are in equivalent (from a energetic point of view) coordination sites. This hypothesis is in agreement with the generally observed tetrahedral geometry for zinc compounds [16]. The thermogravimetric and derivative curves for $ZnCl_2 \cdot 2Imi$ are shown in Fig. 3. The last two mass loss steps are due to the sublimation of the zinc halide formed. The final residue is probably due to the formation of oxo-halide compounds.

The results of the conductance measurements are shown in Table 3. Based on the results obtained

Table 2
Mass loss steps observed in TG curves for imidazole adducts with zinc group halides

Adduct	Mass loss step	Mass loss (%)	ΔT (K)
$ZnCl_2 \cdot 2Imi$	1	45.2	450–690
	2	16.4	690–850
	3	22.5	850–1050
$ZnBr_2 \cdot 2Imi$	1	20.5	605–805
	2	60.3	805–1120
$CdCl_2 \cdot Imi$	1	16.6	493–573
	2	10.7	573–633
	3	71.7	633–973
$CdCl_2 \cdot 2Imi$	1	19.1	403–473
	2	13.1	473–593
	3	8.8	593–633
	4	58.7	633–953
$CdBr_2 \cdot 2Imi$	1	13.9	383–478
	2	16.4	478–583
	3	66.5	583–813
$CdBr_2 \cdot 3Imi$	1	13.6	373–433
	2	14.5	433–473
	3	18.0	473–573
	4	52.5	573–779
$CdI_2 \cdot 2.5Imi$	1	29.9	418–618
	2	69.7	618–738
$HgCl_2 \cdot 2Imi$	1	56.5	433–540
	2	38.5	585–650
$HgBr_2 \cdot 1.5Imi$	1	42.0	433–493
	2	56.4	493–615
$HgI_2 \cdot 1.5Imi$	1	94.5	403–615

ΔT is the temperature range for the thermal degradation process.

Table 3
Conductance measurement results for some imidazole adducts with zinc group halides

Compound	Acetonitrile		Ethanol	
	C	Λ	C	Λ
$ZnCl_2 \cdot 2Imi$	1.01	59.4	1.01	14.8
$ZnBr_2 \cdot 2Imi$	1.01	64.2	0.98	45.0
$CdCl_2 \cdot 2.5Imi$	1.01	108.9	1.00	67.0

C is the compound concentration (10^{-3} mol dm^{-3}) and Λ is the equivalent conductance (Ω^{-1} cm^2 mol^{-1}).

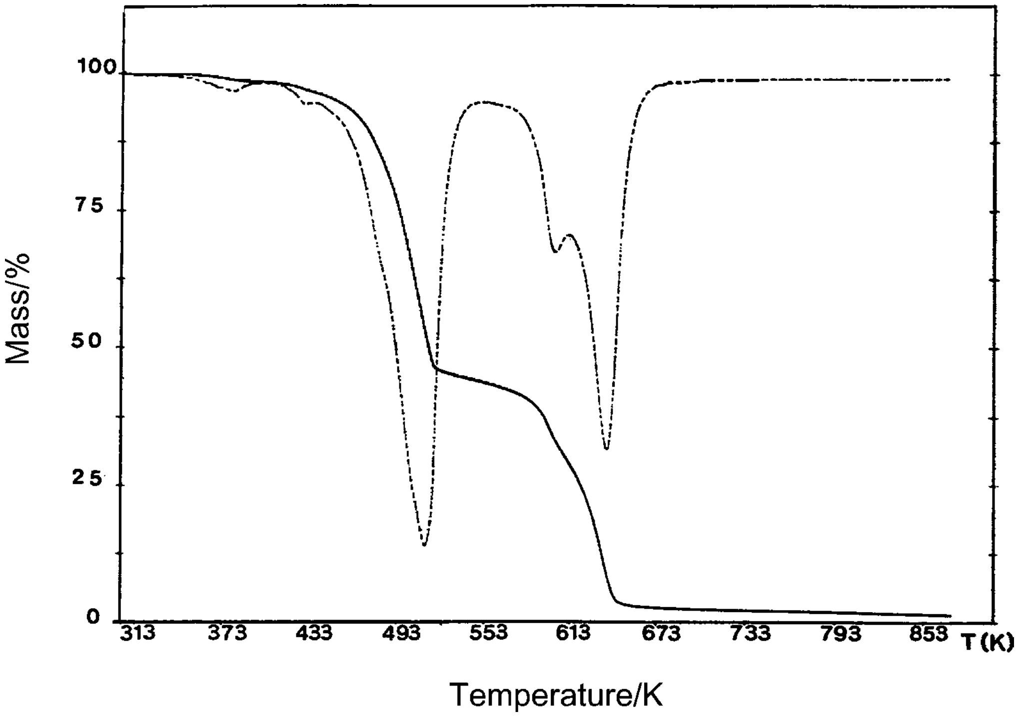

Fig. 2. Thermogravimetric (—) and derivative (–···–) curves for $HgCl_2$·2Imi.

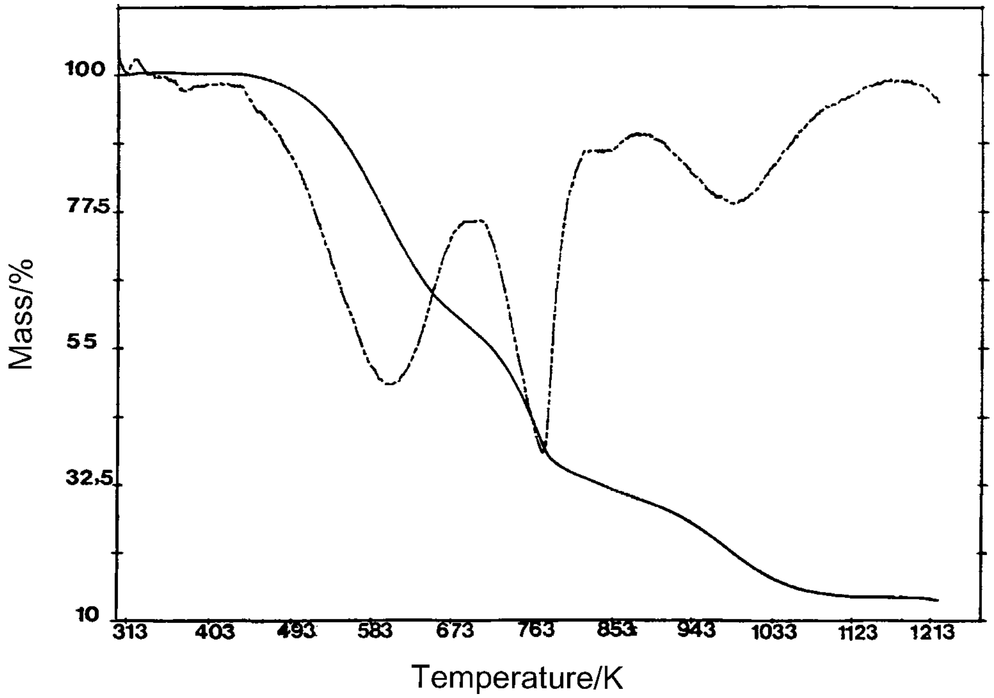

Fig. 3. Thermogravimetric (—) and derivative (–···–) curves for $ZnCl_2$·2Imi.

it can be stated that $ZnCl_2{\cdot}2Imi$ behaves as a non-electrolyte in both solvents, whereas $ZnBr_2{\cdot}2Imi$ is a non-electrolyte in acetonitrile and a 1:1 electrolyte in ethanol. $CdI_2{\cdot}2.5Imi$ is a non-electrolyte in acetonitrile and a 1:2 electrolyte in ethanol [15].

4. Conclusions

Based on the obtained experimental results, some conclusions are as follows:

1. Larger cations, as well as larger anions, induce the presence of a smaller number of imidazole molecules in the coordination sphere of the considered cation.
2. Hard acids exhibit stronger bonds to imidazole than soft acids, and this fact is reflected in the thermal stability sequence.

References

[1] R.F. de Farias, O.A. de Oliveira, J.V. de Medeiros, C. Airoldi, Thermochim. Acta 328 (1999) 241.
[2] R.F. de Farias, H. Scatena Jr., C. Airoldi, J. Inorg. Biochem. 73 (1999) 253.
[3] R.F. de Farias, L.M. Nunes, Transition Met. Chem. 26 (2001) 477.
[4] R.F. de Farias, L. Martínez, C. Airoldi, Thermochim. Acta 376 (2001) 91.
[5] R.F. de Farias, Thermochim. Acta 376 (2001) 63.
[6] R.F. de Farias, C. Airoldi, J. Inorg. Biochem. 76 (1999) 273.
[7] R.F. de Farias, L.M. Nunes, C. Airoldi, J. Thermal Anal. Cal., submitted for publication.
[8] R.F. de Farias, L. Martínez, C. Airoldi, Transition Met. 27 (2002) 253.
[9] R.F. de Farias, G.C. Petrucelli, C. Airoldi, Thermochim. Acta 376 (2001) 1.
[10] R.F. de Farias, C. Airoldi, Thermochim. Acta 378 (2001) 113.
[11] R.F. de Farias, C. Airoldi, Thermochim. Acta 390 (2002) 213.
[12] R.F. de Farias, A.O. da Silva, Transition Met. Chem., in press.
[13] R.F. de Farias, Transition Met. Chem., in press.
[14] R.M. Achelson, Introduction to the Chemistry of Heterocyclic Compounds, Wiley, New York, 1986.
[15] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
[16] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Butterworth-Heinemann, Oxford, 1995.