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Thermochimica Acta 450 (2006) 2–4
thermochimica acta
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Synthesis, characterization and calorimetric study of zinc group halide adducts with aniline

Umberto G. da Silva Jr.[a], Ótom A. de Oliveira[b], Robson F. de Farias[c,*]

[a] *Centro Federal de Educação Tecnológica da Paraíba, Av. 1° de Maio 720, Jaguaribe, João Pessoa, Paraíba, Brazil*
[b] *Departamento de Química, Universidade Federal do Rio Grande do Norte, Cx. Postal 1662, 59078-970 Natal, Rio Grande do Norte, Brazil*
[c] *Departamento de Química, Universidade Federal de Roraima, Cx. Postal 167, 69301-970 Boa Vista, Roraima, Brazil*

Abstract

The adducts $ZnCl_2 \cdot 2an$, $ZnBr_2 \cdot 1.5an$, $CdCl_2 \cdot 2an$, $CdBr_2 \cdot 2an$, $CdI_2 \cdot 2an$, $HgCl_2 \cdot 2an$ and $HgBr_2 \cdot 2an$ (where an = aniline) were synthesized and characterized by elemental analysis, infrared spectroscopy and thermogravimetry and solution calorimetry. Considering the $\Delta_r H_m^\theta$ as well as the $D(M-N)$ values, the following acidity sequence can be established: Zn > Cd > Hg which can be also referring to the hardness of the metal halides. The $\Delta_r H_m^\theta$ values (kJ mol^{-1}) for the reaction MX_2 (c) + nL (l) = $MX_2 \cdot nL$ (c) are: -82.4 ± 3.6 ($ZnCl_2 \cdot 2an$), -77.1 ± 0.4 ($ZnBr_2 \cdot 1.5an$), -45.3 ± 1.4 ($CdCl_2 \cdot 2an$), -45.2 ± 0.7 ($CdBr_2 \cdot 2an$), -60.3 ± 0.1 ($CdI_2 \cdot 2an$) and -41.4 ± 6.3 ($HgCl_2 \cdot 2an$). In the same sequence of compounds, the $D(M-N)$ values (kJ mol^{-1}) are: 143.6, 157.3, 141.2, 126.2, 126.9 and 89.7, respectively.

Keywords: Zinc group halides; Adducts; Thermochemistry

1. Introduction

The research on the thermochemistry of adducts it is still an exciting area taking into account that, as demonstrated by using thermochemical data for zinc adducts, there is a very close relationship between calorimetric, thermogravimetric and infrared spectroscopic data for adducts [1] and so, the thermochemical investigation can provide new insights on the physical–chemical behavior and chemical bonding in such compounds. Furthermore, as verified by using calorimetric data for adducts of zinc and arsenic salts [2,3] calorimetric data can be used to provide more reliable and precise basicity scales, than those provided by only using spectroscopic data [3]. In this connection, and taking into account the different hardness values of the involved metal salts, several group 12 salts adducts have been investigated from a thermochemical point of view [4–6]. The present work is insert in this context and is referring to the synthesis, characterization and calorimetric investigation of the following zinc group halides adducts with aniline: $ZnCl_2 \cdot 2an$, $ZnBr_2 \cdot 1.5an$, $CdCl_2 \cdot 2an$, $CdBr_2 \cdot 2an$, $CdI_2 \cdot 2an$, $HgCl_2 \cdot 2an$ and $HgBr_2 \cdot 2an$, where an = aniline.

2. Experimental

All the reagents used in this work were of analytical grade end they were used without further purification.

All adducts were synthesized by direct mixture of ligand (aniline) and zinc group metal halides. The obtained mixture was then stirred magnetically for time intervals from 0.5 to 5 h. The ligand was added in excess in order to guarantee the “saturation” of the coordination sphere of the metal cation. The compounds $CdI_2 \cdot 2an$ and $HgCl_2 \cdot 2an$ were aged for 30 and 10 days, respectively. The formed compounds were washed with ethyl ether and dried under vacuum at room temperature.

The metal and halide contents were determined by complexometric EDTA titration and potentiometric $AgNO_3$ titration, respectively. The melting point intervals were measured in a Quimis Metrohm Herisau equipment. The thermogravimetric curves were obtained in a TGA 7 Perkin-Elmer equipment with a nitrogen flow of 17 cm^3 min^{-1} atmosphere and a heating rate of 10 °C min^{-1}. The infrared spectra were obtained in KBr matrix in the 4000–200 cm^{-1} range by using a Perkin-Elmer equipment model 16 FPC-IR.

The calorimetric measurements were performed by using a isoperibolic calorimeter constructed in the Department of Chemistry of the Universidade Federal do Rio Grande do Norte that

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* Corresponding author. Tel.: +55 95 81118206.
E-mail address: robsonfarias@pesquisador.cnpq.br (R.F. de Farias).

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doi:10.1016/j.tca.2006.04.010

has been previously described [6]. Ethanol was employed as calorimetric solvent.

To obtain the energetic information about the prepared adducts, a complete set of thermochemical parameters were calculated. The standard molar reaction enthalpy in condensed phase: MX_2 (cr) + nL (cr) = $MX_2 \cdot nL$ (cr); $\Delta_r H_m^\theta$, can be calculated by using the following thermochemical cycle:

$$MX_2\,(cr) + \text{solvent} = \text{Sol A}; \qquad \Delta_1 H_m^\theta$$

$$\text{Sol A} + nL\,(cr) = \text{Sol B}; \qquad \Delta_2 H_m^\theta$$

$$MX_2 \cdot nL\,(cr) + \text{solvent} = \text{Sol C}; \qquad \Delta_3 H_m^\theta$$

$$\text{Sol A} = \text{Sol C}; \qquad \Delta_4 H_m^\theta$$

In each calorimetric reaction a strict control of stoichiometry was maintained to ensure an equivalence of the initial and final stages of the reactions. Since the thermodynamic state of the second and third reactions is the same, the value for $\Delta_4 H_m^\theta$ is zero. So, $\Delta_r H_m^\theta$ can be calculated by Hess's law, through the equation: $\Delta_r H_m^\theta = \Delta_1 H_m^\theta + \Delta_2 H_m^\theta - \Delta_3 H_m^\theta$.

The values for the enthalpy of decomposition ($\Delta_D H_m^\theta$) and the lattice enthalpy ($\Delta_M H_m^\theta$) which corresponded to the following reactions: $MX_2 \cdot nL$ (cr) = MX_2 (cr) + nL (g); $MX_2 \cdot nL$ (cr) = MX_2 (g) + nL (g), respectively, were calculated applying the equations: $\Delta_D H_m^\theta = -\Delta_r H_m^\theta + n\Delta_{cr}^{g} H_m^\theta$ (L) and $\Delta_M H_m^\theta = \Delta_D H_m^\theta + \Delta_{cr}^{g} H_m^\theta$ (MX_2). The acid–base enthalpy reaction in the gaseous phase, $\Delta_g H_m^\theta$, according to the reaction: MX_2 (g) + nL (g) = $MX_2 \cdot nL$ (g), can be calculated by the expression: $\Delta_g H_m^\theta = \Delta_M H_m^\theta + \Delta_{cr}^{g} H_m^\theta$ (L) [7]. From the $\Delta_g H_m^\theta$ values the mean metal-ligand bond dissociation enthalpy can be calculated through the expression: $< D >$ (M-L) $= \Delta_g H_m^\theta / n$, where n is the number of ligands [7].

As auxiliary data for the calculations, the following enthalpies of sublimation (kJ mol^{-1}) were considered: $ZnCl_2$ (149), $ZnBr_2$ (131), $CdCl_2$ (181.2), $CdBr_2$ (151.5), CdI_2 (137.7), $HgCl_2$ (82.2) and $HgBr_2$ (84.2) [8] and the vaporization enthalpy of aniline (55.8) [9].

3. Results and discussion

The experimental analytical data are in good agreement (±3%) with the proposed general formulas. The measured melting points intervals, general formulas and the main infrared absorption bands for aniline and its compounds with the zinc group halides are shown in Table 1. As can be verified, the cadmium chloride and cadmium bromide adducts are the most stable from a thermal point of view, suggesting that, for these compounds, the intermolecular forces are stronger than to the other ones. Such fact could be related with the fact that many cadmium compounds polymerize [10].

The negative shifts observed for several bands are indicative of coordination trough nitrogen of the ligand [11].

Table 1
Melting temperatures and main infrared bands (cm^{-1}) for aniline and its adducts with group 12 halides

Compound	Melting temperature (°C)	$\nu(NH)_{as}$	$\nu(NH)_s$	ν(M–N)	ν(M–X)	ν(CN)
An	–	3448–3390	3226	–	–	1274
$ZnCl_2 \cdot 2an$	258–265	3262	3220	406–362	294–272	1218
$ZnBr_2 \cdot 1.5an$	260–266	3262	3218	402–356	230–245	1216
$CdCl_2 \cdot 2an$	>321	3340	3292	374–302	218–226	1240
$CdBr_2 \cdot 2an$	>321	3306	3244	366–318	–	1238
$CdI_2 \cdot 2an$	175–184	3298	3234	370	–	1227
$HgCl_2 \cdot 2an$	141–143	3584	3526	396	206	1270
$HgBr_2 \cdot 2an$	107–108	3526	3282	365	203	1218

Table 2
Thermogravimetric results for group 12 halide adducts with aniline

Compound	Temperature interval (°C)	Mass loss/%calc. (exp.)	Process
$ZnCl_2 \cdot 2an$	110–362	57.8 (54.9)	$ZnCl_2 \cdot 2an$ (s) → $ZnCl_2$ (s) + 2an (g)
	362–448	42.3 (29.7)	$ZnCl_2$ (s) → $ZnCl_2$ (g)
$ZnBr_2 \cdot 1.5an$	115–217	38.3 (37.5)	$ZnBr_2 \cdot 1.5an$ (s) → $ZnBr_2$ (s) + 3/2an (g)
	244–416	61.7 (62.1)	$ZnBr_2$ (s) → $ZnBr_2$ (g)
$CdCl_2 \cdot 2an$	32–293	50.4 (53.4)	$CdCl_2 \cdot 2an$ (s) → $CdCl_2$ (s) + 2an (g)
	293–700	49.6 (46.0)	$CdCl_2$ (s) → $CdCl_2$ (g)
$CdBr_2 \cdot 2an$	39–221	40.6 (40.6)	$CdBr_2 \cdot 2an$ (s) → $CdBr_2$ (s) + 2an (g)
	221–648	59.4 (59.0)	$CdBr_2$ (s) → $CdBr_2$ (g)
$CdI_2 \cdot 2an$	30–280	37.7 (33.7)	$CdI_2 \cdot 2an$ (s) → CdI_2 (s) + 2an (g)
	280–650	66.3 (66.)	CdI_2 (s) → CdI_2 (g)
$HgCl_2 \cdot 2an$	42–201	87.8 (76.1)	$HgCl_2 \cdot 2an$ (s) → $HgCl_2$ (g) + 2an (g) and/or $HgCl_2 \cdot 2an$ (s) → $gCl_2 \cdot 2an$ (g)
$HgBr_2 \cdot 2an$	39–156	97.7 (97.6)	$HgBr_2 \cdot 2an$ (s) → $HgBr_2$ (g) + 2an (g) and/or $HgBr_2 \cdot 2an$ (s) → $HgBr_2 \cdot 2an$ (g)

Table 3
Dissolution enthalpies for group 12 halide adducts with aniline

Process	$\Delta H_{diss.}$ (kJ mol^{-1})
an (l) + EtOH → an (sol)	0.24 ± 0.06
$ZnCl_2$ (s) + an (sol) → $ZnCl_2$·2an (sol)	−46.70 ± 0.58
$ZnBr_2$ (s) + 3/2an (sol) → $ZnBr_2$·1.5an (sol)	−53.18 ± 0.14
$ZnCl_2$·2an (s) + EtOH → $ZnCl_2$·2an (sol)	−36.05 ± 3.57
$ZnBr_2$·1.5an (s) + $ZnBr_2$·1.5an (sol)	−24.25 ± 0.39
$CdCl_2$ (s) + 2an (sol) → $CdCl_2$·2an (sol)	−2.28 ± 0.33
CdI_2 (s) + 2an (sol) → CdI_2.2an (sol)	−7.58 ± 0.30
$CdBr_2$ (s) + 2an (sol) → $CdBr_2$·2an (sol)	−12.45 ± 0.84
$CdCl_2$·2an (s) + EtOH → $CdCl_2$·2an (sol)	−43.39 ± 1.33
$CdBr_2$·2an (s) + EtOH → $CdBr_2$·2an (sol)	−37.93 ± 0.64
CdI_2·2an (s) + EtOH → CdI_2·2an (sol)	−48.23 ± 0.50
$HgCl_2$ (s) + 2an (sol) → $HgCl_2$·2an (sol)	−4.47 ± 0.27
$HgCl_2$·2an (s) + EtOH → $HgCl_2$·2an (sol)	−46.16 ± 0.34

Table 4
Thermochemical parameters for group 12 halide adducts with aniline

	$\Delta_r H^{\theta}_{m}$	$\Delta_D H^{\theta}_{m}$	$\Delta_M H^{\theta}_{m}$	$\Delta_g H^{\theta}_{m}$	$D(M-N)$
$ZnCl_2$·2an	−82.4 ± 3.6	194	−343.0	−287.2	143.6
$ZnBr_2$·1.5an	−77.1 ± 0.4	160.8	−291.8	−236.0	157.3
$CdCl_2$·2an	−45.3 ± 1.4	156.9	−338.1	−282.3	141.2
$CdBr_2$·2an	−45.2 ± 0.7	156.8	−308.3	−252.5	126.2
CdI_2·2an	−60.3 ± 0.1	171.9	−309.6	−253.8	126.9
$HgCl_2$·2an	−41.4 ± 6.3	153.0	−235.2	−179.4	89.7

A summary of the thermogravimetry data are shown in Table 2. In all compounds the elimination of ligand molecules occurs in a single step of mass lost. This suggests that, from an energetic point of view, the two ligand molecules are located at energetically equivalent coordination sites. With the exception of zinc chloride, all salts sublimate completely after the release of ligand molecules. For $ZnCl_2$ the final residue is composed by zinc oxychloride. For mercury compounds which exhibit a large single step of mass loss, two phenomena are possible: the simultaneous release of gaseous aniline molecules and mercury halide sublimation, or the sublimation of the mercury halide-aniline compound itself.

The thermochemical data are summarized in Tables 3 and 4. For the cadmium halide adducts the metal-ligand bond enthalpy is greater for the chloride compound and that the Br and I compounds exhibits very closer metal-ligand enthalpy values.

The infrared data (Table 1) shown that for cadmium adducts, the $\nu(NH)_{as}$ band exhibits "progressive" negative (cm^{-1}) with respect to the free ligand from Cl to I: 3340 (Cl), 3306 (Br) and 3298 (I), and that the Br and I compounds exhibit very close shift values. So, it is possible that larger negative shifts of the $\nu(NH)_{as}$ band are associated with weaker metal-ligand bonds. The same hypothesis it can be pointed out for the $\nu(NH)_{s}$ band.

Based on the dissolution enthalpy values shown in Table 3. The cadmium halides adducts are those with higher dissolution enthalpy, suggesting that these compounds exhibit higher intermolecular forces, as also suggested by the melting temperatures. On the other hand, comparing only the chloride compounds, can be verified that the dissolution enthalpy values follows the sequence: Hg > Cd > Zn.

Considering the $\Delta_r H^{\theta}_{m}$ as well as the $D(M-N)$ values in Table 4, the following acidity sequence for the halides can be established: Zn > Cd > Hg which is also related with the hardness of the metal halides. That is, higher $\Delta_r H^{\theta}_{m}$ and $D(M-N)$ values are related with harder metal halides. Considering only the cadmium adducts, the higher $\Delta_r H^{\theta}_{m}$ value is observed for the iodide compound, that is, larger and softer anions favor higher values of $\Delta_r H^{\theta}_{m}$, probably due to the fact that higher anions allows a better insertion of the ligand into the crystalline network of the metal salt. Such better insertion is not related, apparently, with a shorter metal-ligand distance, since from Br to I compounds, higher values of $\Delta_r H^{\theta}_{m}$are not associated with higher values of $D(M-N)$.

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