

Thermogravimetric and calorimetric study of cadmium iodide adducts with cyclic ureas

Robson F. de Farias*, Claudio Airoidi

Instituto de Química, Universidade Estadual de Campinas CP 6154, 13083-970 Campinas, Sao Paulo, Brazil

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Abstract

Adducts of general formula $\text{CdI}_2 \cdot n\text{L}$ [$n = 1$ and 2 ; L: ethyleneurea (eu) and propyleneurea (pu)] were synthesized by a solid state route and characterized by elemental analysis, infrared spectroscopy, thermogravimetry and reaction solution calorimetry. The infrared results shown that eu and pu coordinate through oxygen atom. All adducts release the ligand molecules in a single mass loss step, suggesting that, in the bisadducts, both ligand molecules are in equivalent coordination sites, exhibiting similar bond enthalpies. For all thermogravimetric curves, the first mass loss step is associated with the release of ligand molecules and the second one with the sublimation of cadmium iodide: $\text{CdI}_2 \cdot n\text{L}(\text{s}) \rightarrow \text{CdI}_2(\text{s}) + n\text{L}(\text{g})$; $\text{CdI}_2(\text{s}) \rightarrow \text{CdI}_2(\text{g})$. The observed thermal stability trend is: $\text{CdI}_2 \cdot \text{eu}$ (228°C) $>$ $\text{CdI}_2 \cdot \text{pu}$ (213°C) $>$ $\text{CdI}_2 \cdot 2\text{pu}$ (200°C) $>$ $\text{CdI}_2 \cdot 2\text{eu}$ (186°C). The standard molar reaction enthalpy in condensed phase: $\text{CdI}_2(\text{cr}) + n\text{L}(\text{cr}) = \text{CdI}_2 \cdot n\text{L}(\text{cr})$; $\Delta_r H_m^\ominus$, were obtained from reaction-solution calorimetry, to give the following values for mono and bisadducts: -7.16 and -27.61 , -4.99 and $-9.07 \text{ kJ mol}^{-1}$ for eu and pu adducts, respectively. Decomposition ($\Delta_D H_m^\ominus$) and lattice ($\Delta_M H_m^\ominus$) enthalpies, as well as the mean cadmium–oxygen bond dissociation enthalpy, $D(\text{Cd}–\text{O})$, were calculated for all adducts.

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1. Introduction

Cadmium chemistry is an important area of research from an environmental point of view [1] due to its toxic effects on a wide variety of living organism, including man. On the other hand, unlike zinc, cadmium does not appear to play any role as an essential trace element [2].

A review dealing with the structural determination of over 600 cadmium complexes was recently published [3]. The cadmium complexes studied exhibited coordination numbers ranging from 2 to 8, including a 2-imidazolidinone (ethyleneurea) complex with coordination number 6.

Ethyleneurea (eu) and propyleneurea (pu), whose structures are shown in Fig. 1, have been used as ligands to produce adducts with a large variety of divalent metals such as zinc [4], copper [5], cadmium [6] cobalt [7], tin [8], nickel [9] and cerium [9]. Such ligands were used mainly due to their similarity to many molecules of biological interest. On the other hand, it has been shown that thermo-

gravimetry and solution calorimetry are reliable tools to study metal–aminoacids interactions, [10–14], as well as the coordinative features of metals to molecules of biological interest such as imidazole [15,16] and caffeine [17].

The aim of this article is to report the calorimetric and thermogravimetric study for adducts of general formula $\text{CdI}_2 \cdot n\text{L}$, where $n = 1$ and 2 ; L: eu and pu.

2. Experimental

All adducts were synthesized through a solid state route by grinding stoichiometric amounts of the metal halides and ligands in a mortar for 70 min, at room temperature.

Infrared spectra obtained for free ligands and adducts confirms that there are no free ligand molecules after the grinding process. The synthesized adducts were dried under vacuum at room temperature for 24 h.

C, H and N elemental analysis were performed in a Perkin-Elmer analyzer. Infrared spectra were recorded in a Bomem apparatus in the $4000\text{--}400 \text{ cm}^{-1}$ range, with a resolution of 4 cm^{-1} . All IR spectra were obtained from

* Corresponding author. Fax: +55-19-3788-3109.

E-mail address: robsonfarias@aol.com (R.F. de Farias).

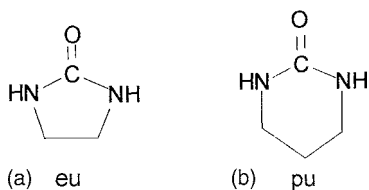


Fig. 1. Structural formulas of ethyleneurea (a) and propyleneurea (b).

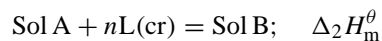
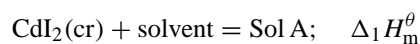
powders in KBr discs. Thermogravimetric curves were obtained using a Shimadzu TGA 50 apparatus under Ar atmosphere with a heating rate of $5^{\circ}\text{C min}^{-1}$.

Calorimetric measurements were carried out on a Thermometric isoperibolic instrument, model LKB 2250, by using ampoule breaking procedure. All measurements were taken at 298.15 ± 0.02 K, using a 0.10 dm^3 reaction vessel, charged with the calorimetric solvent (deionized water).

For each enthalpic determination, at least six individual ampoules were broken and the complete thermal effects were recorded during 300 s. Ampoules of cadmium iodide and

adducts were prepared under anhydrous conditions under nitrogen atmosphere. Uncertainty intervals associated with the variation of the enthalpies of solution are quoted as twice of the standard deviation of the mean.

To obtain the energetic information about the cadmium–amide interactions, a complete set of thermochemical parameters were obtained. The standard molar enthalpy of reaction in condensed phase: $\text{CdI}_2(\text{cr}) + n\text{L}(\text{cr}) = \text{CdI}_2 \cdot n\text{L}(\text{cr})$; $\Delta_r H_m^\theta$, can be calculated by using the following thermochemical cycle:



In each calorimetric reaction, a strict control of stoichiometry was maintained to ensure an equivalence of the initial and final stages of the reactions. A null enthalpy $\Delta_4 H_m^\theta$ was obtained when ampoules of mixtures of reactants were

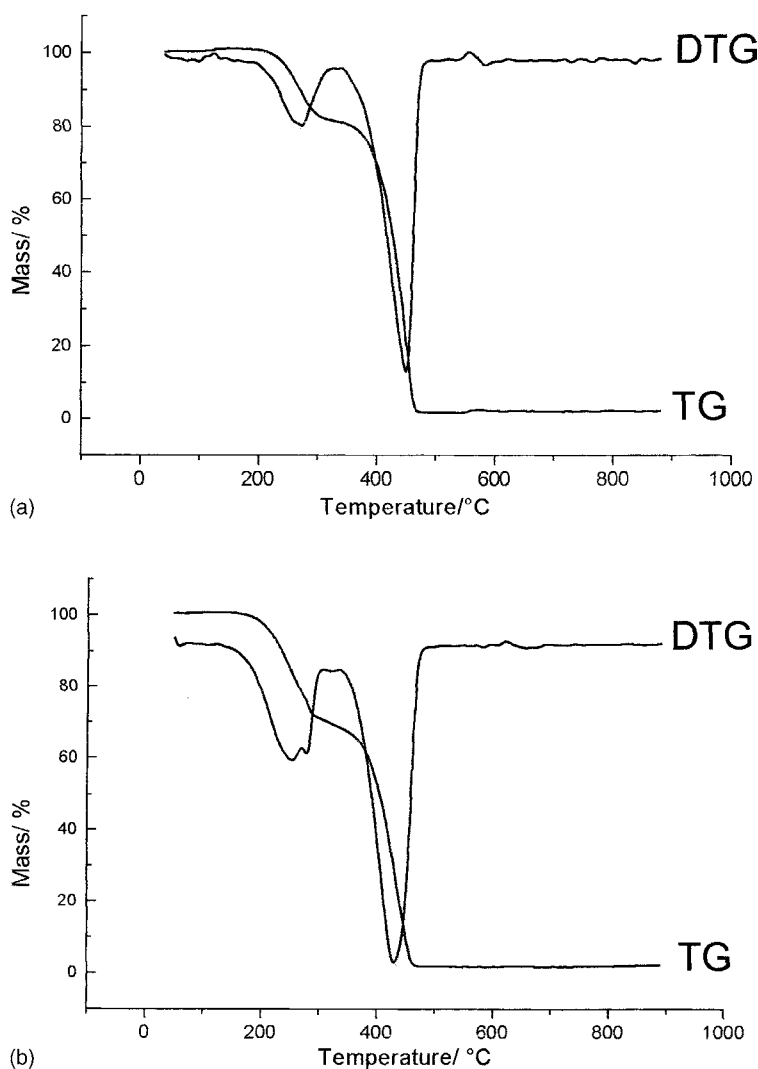
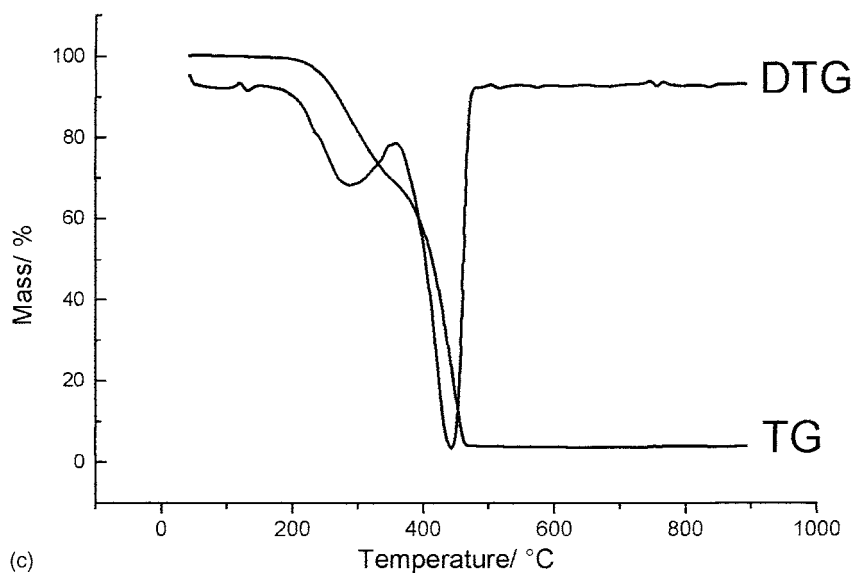
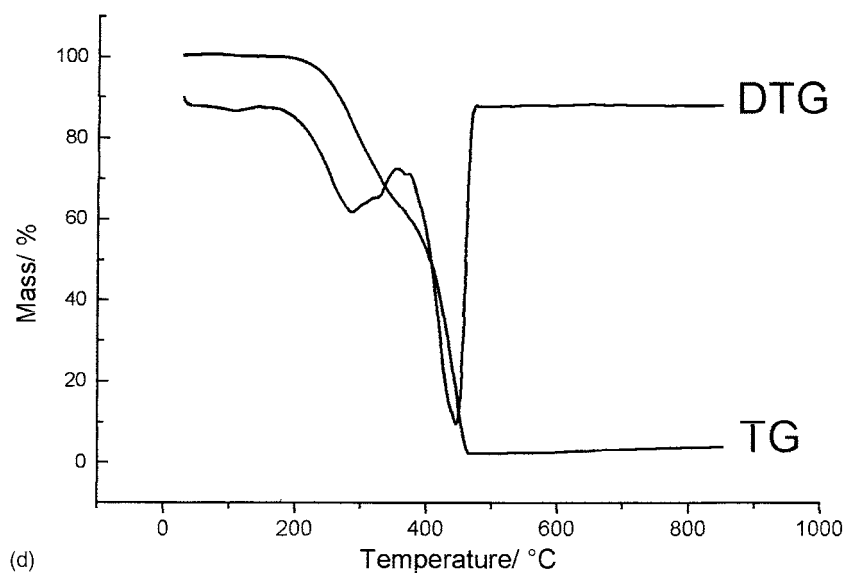


Fig. 2. Thermogravimetric (TG) and derivative (DTG) curves for: CdI_2 -eu (a), $\text{CdI}_2 \cdot 2\text{eu}$ (b), CdI_2 -pu (c) and $\text{CdI}_2 \cdot 2\text{pu}$ (d).



(c)



(d)

Fig. 2. (Continued).

broken into a solution of the product. 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: $\text{CdI}_2 \cdot n\text{L}(\text{cr}) = \text{CdI}_2(\text{cr}) + n\text{L}(\text{g})$; $\text{CdI}_2 \cdot n\text{L}(\text{cr}) = \text{CdI}_2(\text{g}) + n\text{L}(\text{g})$, respectively, were calculated applying the equations: $\Delta_D H_m^\theta = -\Delta_r H_m^\theta + n\Delta_{\text{cr}}^{\text{g}} H_m^\theta(\text{L})$ and $\Delta_M H_m^\theta = \Delta_D H_m^\theta + \Delta_{\text{cr}}^{\text{g}} H_m^\theta(\text{CdI}_2)$. The acid–base enthalpy reaction in gaseous phase, $\Delta_g H_m^\theta$, which enthalpic value corresponded to $\text{CdI}_2(\text{g}) + n\text{L}(\text{g}) = \text{CdI}_2 \cdot n\text{L}(\text{g})$, can be calculated by the expression: $\Delta_g H_m^\theta = \Delta_M H_m^\theta - \Delta_{\text{cr}}^{\text{g}} H_m^\theta(\text{L})$. From the $\Delta_g H_m^\theta$ values, the mean metal–ligand bond dissociation enthalpy can be calculated through the expression: $\langle D \rangle (\text{M-L}) = \Delta_g H_m^\theta / n$, where n is the number of ligands.

As auxiliary data for the calculations, the enthalpies of sublimation for cadmium iodide, eu and pu were used as $137.7 \text{ kJ mol}^{-1}$ [18], $83.7 \pm 1.9 \text{ kJ mol}^{-1}$ [4] and $89.3 \pm 2.5 \text{ kJ mol}^{-1}$ [4], respectively.

3. Results and discussion

The CHN elemental analysis results are summarized in Table 1. The main infrared bands for free ligands and adducts are summarized in Table 2. The obtained elemental analysis results are in good agreement with the proposed formulas.

For cyclic ureas, such as eu and pu, a decrease in the carbonyl stretching frequency associated with an increase for both, amide II and C–N stretching bands, are evidences

Table 1

Elemental analysis for adducts of general formula $\text{CdI}_2 \cdot n\text{L}$ ($n = 1$ and 2 ; L: eu and pu). Calculated values are in parenthesis

Adduct	C	H	N
$\text{CdI}_2 \cdot \text{eu}$	8.15 (7.96)	1.56 (1.33)	5.90 (6.20)
$\text{CdI}_2 \cdot 2\text{eu}$	13.80 (13.38)	2.28 (2.23)	10.41 (10.41)
$\text{CdI}_2 \cdot \text{pu}$	10.73 (10.29)	1.85 (1.72)	6.21 (6.00)
$\text{CdI}_2 \cdot 2\text{pu}$	16.50 (16.96)	2.77 (2.83)	9.85 (9.90)

Table 2

Main IR bands (cm^{-1}) for ethyleneurea, propyleneurea and the adducts of general formula $\text{CdI}_2 \cdot n\text{L}$ ($n = 1$ and 2 ; L: eu and pu)

Compound	Amide I $\nu(\text{C}=\text{O})$	Amide II (N–H)	$\nu(\text{C}-\text{N})$
eu	1685	1508	1274
$\text{CdI}_2 \cdot \text{eu}$	1679	1498	1277
$\text{CdI}_2 \cdot 2\text{eu}$	1677	1498	1276
pu	1690	1542	1312
$\text{CdI}_2 \cdot \text{pu}$	1671	1542	1314
$\text{CdI}_2 \cdot 2\text{pu}$	1637	1542	1313

of coordination through oxygen [4,5]. Hence, can concluded that for eu and pu the coordination occurs through oxygen.

The mass loss percentages due to the release of ligand molecules, as calculated by using the TG curves, are in agreement with the elemental analysis results in a range of $\pm 5\%$. All adducts release the ligand molecules in a single mass loss step, suggesting that, in the bisadducts, both ligand molecules are in equivalent coordination sites exhibiting similar bond enthalpies. The obtained thermogravimetric curves are shown in Fig. 2. For all thermogravimetric curves, the first mass loss step is associated with the release of ligand molecules and the second one with the sublimation of cadmium iodide: $\text{CdI}_2 \cdot n\text{L}(\text{s}) \rightarrow \text{CdI}_2(\text{s}) + n\text{L}(\text{g})$; $\text{CdI}_2(\text{s}) \rightarrow \text{CdI}_2(\text{g})$.

The observed thermal stability trend is: $\text{CdI}_2 \cdot \text{eu}$ (228°C) $>$ $\text{CdI}_2 \cdot \text{pu}$ (213°C) $>$ $\text{CdI}_2 \cdot 2\text{pu}$ (200°C) $>$ $\text{CdI}_2 \cdot 2\text{eu}$ (186°C), and so, the bisadducts are less stable than monoadducts.

The enthalpic values for all dissolution processes employed in the thermodynamic cycle are listed in Table 3. Each enthalpic value of dissolution is a mean value of at least five independent measurements. A complete set of thermochemical parameters is presented in Table 4.

Table 3

Dissolution enthalpy values (kJ mol^{-1}) for the dissolution steps involved in the calculation of $\Delta_r H_m^\theta$.

Adduct	$\Delta_1 H_m^\theta$	$\Delta_2 H_m^\theta$	$\Delta_3 H_m^\theta$
$\text{CdI}_2 \cdot \text{eu}$	10.05 ± 10.04	12.07 ± 10.02	29.28 ± 0.01
$\text{CdI}_2 \cdot 2\text{eu}$	10.05 ± 10.04	12.23 ± 10.01	49.89 ± 10.01
$\text{CdI}_2 \cdot \text{pu}$	10.05 ± 10.04	13.60 ± 10.01	28.64 ± 10.01
$\text{CdI}_2 \cdot 2\text{pu}$	10.05 ± 10.04	13.70 ± 10.01	32.82 ± 10.14

Table 4

Thermochemical parameters (kJ mol^{-1}) for the adducts $\text{CdI}_2 \cdot n\text{L}$

Adduct	$-\Delta_r H_m^\theta$	$\Delta_D H_m^\theta$	$\Delta_M H_m^\theta$	$-\Delta_g H_m^\theta$	$D(\text{Cd}-\text{O})$
$\text{CdI}_2 \cdot \text{eu}$	7.16 ± 10.05	90.86	228.56	144.86	144.86
$\text{CdI}_2 \cdot 2\text{eu}$	27.61 ± 10.04	195.01	332.71	249.01	124.05
$\text{CdI}_2 \cdot \text{pu}$	4.99 ± 10.04	94.29	232.00	142.70	142.70
$\text{CdI}_2 \cdot 2\text{pu}$	9.07 ± 10.15	187.67	325.37	236.07	118.05

4. Conclusions

Based on Tables 3 and 4 data, the following conclusions could be pointed out:

- (1) Ethyleneurea adducts exhibit with larger dissolution enthalpies in comparison with pu ones. This fact suggests stronger intermolecular forces for those compounds.
- (2) The abnormally high dissolution and $\Delta_r H_m^\theta$ enthalpy values obtained for $\text{CdI}_2 \cdot 2\text{eu}$ suggests that for this compound, the intermolecular forces are the strongest between the considered adducts, probably due to some specific structural feature.
- (3) The $D(\text{Cd}-\text{O})$ values are larger for the monoadducts, which is a reasonable achievement, taking into account that, in the bisadducts, there are two ligand molecules providing electronic density for the metal cation, resulting in a weaker bond formation with each individual ligand molecule.
- (4) The $D(\text{Cd}-\text{O})$ values are larger for eu adducts. This behavior was not observed for copper adducts with eu and pu [19], for which a larger Cu–pu bond enthalpy value is calculated.
- (5) Based on the $\Delta_r H_m^\theta$ values, the basicity sequence could be established as eu $>$ pu. The same conclusion is obtained based on $\langle \text{Cd}-\text{O} \rangle$ values.
- (6) Dissolution enthalpies for CdI_2 adducts are larger than those observed for CdCl_2 adducts with the same ligands [20], suggesting stronger intermolecular interactions for the former.
- (7) The mean cadmium–oxygen bond enthalpies are larger for CdCl_2 adducts with eu and pu [20] in comparison with values calculated for CdI_2 adducts with the same ligands. Such a fact could be explained taking into account the different hardness of the halides ions, with Cl^- been a hard base, whereas I^- is a soft. Thus, I^- interacts most effectively with Cd^{2+} (a borderline acid) than Cl^- , and the consequence is a weaker $\text{Cd}^{2+}-\text{O}$ interaction.

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