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Short communication

Calorimetric study of the adducts $CdBr_2 \cdot nL$ ($n = 1$ and 2; L = ethyleneurea and propyleneurea)

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Abstract

A calorimetric study was performed for adducts of general formula $CdBr_2 \cdot nL$ ($n = 1$ and 2; L = ethyleneurea (eu) and propyleneurea (pu)). The standard molar reaction enthalpy in condensed phase: $CdBr_2(c) + nL(c) = CdBr_2 \cdot nL(c)$; $\Delta_r H^{\theta}_m$, were obtained by reaction–solution calorimetry, to give the following values for mono- and bis-adducts: −19.54 and −34.59; −7.77 and −19.05 kJ mol^{-1} for eu and pu adducts, respectively. Decomposition ($\Delta_D H^{\theta}_m$) and lattice ($\Delta_M H^{\theta}_m$) enthalpies, as well as the mean cadmium–oxygen bond dissociation enthalpy, $D\langle$Cd–O$\rangle$, were calculated for all adducts.

Keywords: Adducts; Cadmium bromide; Calorimetry; Amides

1. Introduction

Taking into account their similarity to many molecules of biological interest, ethyleneurea (eu) and propyleneurea (pu), whose structures are shown in Fig. 1, have been used as ligands for the synthesis of coordination compounds with zinc [1], copper [2], cadmium [3], cobalt [4] and tin [5] salts.

Thermal techniques, such as thermogravimetry and solution calorimetry, have been successfully employed for the study of the energetics of interactions of metal cations with biological species, such as amino acids [6–9].

The aim of this article is to report the calorimetric study of adducts of general formula $CdBr_2 \cdot nL$, where $n = 1$ and 2, and L = eu and pu.

2. Experimental

Adducts of the general formula $CdBr_2 \cdot nL$ (where $n = 1$ and 2, and L = eu and pu), were synthesized and characterized as previously described [3]. All calorimetric measurements and calculations were performed as described elsewhere [10]. As auxiliary data for the calculations, the enthalpies of sublimation for cadmium bromine, eu and pu were used as 151.5 [11], 83.7 ± 1.9 [1] and 89.3 ± 2.5 kJ mol^{-1} [1], respectively.

3. Results and discussion

The CHN elemental analysis and infrared results were previously reported [3]. The infrared data shows 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 obtained

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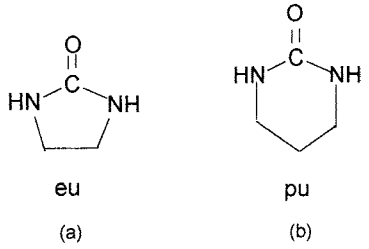

Fig. 1. Structures of eu and pu.

TG curves [3], are in agreement with the elemental analyses results in a range of ±2%. All adducts release the ligand molecules in a single mass loss step, suggesting that, in the bis-adducts, both ligand molecules are in equivalent coordination sites, exhibiting similar bond enthalpies. In considering adducts with the same stoichiometry, the observed thermal stability trend is: pu > eu, and bis-adducts are less stable than mono-adducts.

The enthalpic values for all dissolution processes employed in the thermodynamic cycle are listed in Table 1. 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 2. Based on the data in Tables 1 and 2, we conclude:

1. Ethyleneurea adducts exhibit larger dissolution enthalpies than propyleneurea adducts. This fact strongly suggests that the intermolecular forces for eu adducts are stronger than for pu adducts. This agrees with the calculated larger lattice enthalpy values for eu adduts.
2. The $D\langle$Cd–O$\rangle$ values are larger for the mono-adducts, which is a reasonable, taking into account that, in the bis-adducts, there are two ligand molecules providing electronic density for the metal cation, resulting in a weaker bond.
3. The $D\langle$Cd–O$\rangle$ values are larger for eu adducts. This behavior was not observed for copper adducts with eu and pu [12], for which a larger Cu–pu bond enthalpy value is calculated.
4. Ethyleneurea adducts, which exhibit the larger decomposition enthalpy values, are not the most stable ones from a thermic point of view, as proved by TG analysis.
5. Based on the $\Delta_r H^\theta_m$ values, the basicity sequence could be established as eu > pu. The same conclusion is obtained based on $\langle$Cd–O$\rangle$ values.
6. Dissolution enthalpies for $CdBr_2$ adducts are larger than those observed for $CdCl_2$ adducts with the same ligands [10], suggesting stronger intermolecular interactions in the former.
7. The mean cadmium–oxygen bond enthalpies are larger for $CdCl_2$ adducts with eu and pu [10] in comparison with values calculated for $CdBr_2$ adducts with the same ligands. This fact could be explained by the different hardness of the halides ions, with Cl^- been a hard base, whereas Br^- is a borderline one. Thus, Br^- interacts most effectively with Cd^{2+} (a borderline acid) than Cl^-, giving as a consequence, weaker Cd^{2+}–O interactions.

Table 1
Dissolution enthalpy values (kJ mol^{-1}) for the dissolution steps involved in the calculation of $\Delta_r H^\theta_m$

Adduct	$\Delta_1 H^\theta_m$	$\Delta_2 H^\theta_m$	$\Delta_3 H^\theta_m$
$CdBr_2$·eu	−5.19 ± 0.01	12.21 ± 0.01	26.56 ± 0.01
$CdBr_2$·2eu	−5.19 ± 0.01	12.37 ± 0.01	41.77 ± 0.01
$CdBr_2$·pu	−5.19 ± 0.01	13.01 ± 0.01	15.59 ± 0.01
$CdBr_2$·2pu	−5.19 ± 0.01	13.74 ± 0.01	27.60 ± 0.01

Table 2
Thermochemical parameters (kJ mol^{-1}) for the adducts $CdCl_2$·nL

Adduct	$-\Delta_r H^\theta_m$	$\Delta_D H^\theta_m$	$\Delta_M H^\theta_m$	$-\Delta_g H^\theta_m$	$D\langle$M–L$\rangle$
$CdBr_2$·eu	19.54 ± 0.02	103.2	254.7	171	171
$CdBr_2$·2eu	34.59 ± 0.02	202.0	353.5	269.8	134.9
$CdBr_2$·pu	7.77 ± 0.02	97.1	248.6	159.3	159.3
$CdBr_2$·2pu	19.05 ± 0.02	197.7	349.2	259.9	130.0

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