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Calorimetric study of ethyleneurea, ethylenethiourea and propyleneurea cadmium chloride adducts

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Abstract

Adducts of the general formula $CdCl_2{\cdot}nL$ [$n = 1$ and 2; L = ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu)] were synthesized by a solid state route and characterized by elemental analysis, infrared spectroscopy, and reaction solution calorimetry. The infrared results showed that eu and pu coordinate through carbonylic oxygen atoms, whereas etu uses the nitrogen as coordinating site. The standard molar reaction enthalpy in condensed phase: $CdCl_2(c) + nL(c) = CdCl_2{\cdot}nL(c)$; $\Delta_r H^{\theta}_m$, were obtained from reaction–solution calorimetry, to give the following values for mono and bisadducts: -20.0 ± 0.1; -19.9 ± 0.1; -13.3 ± 0.1 and -38.6 ± 0.1; -56.9 ± 0.1; -17.0 ± 0.1 kJ mol^{-1} for eu, etu and pu, respectively. The values of decomposition ($\Delta_D H^{\theta}_m$) and lattice enthalpy ($\Delta_M H^{\theta}_m$) as well as the mean cadmium–ligand bond dissociation enthalpy, D(Cd–L), were calculated for all adducts.

Keywords: Adducts; Cadmium chloride; Calorimetry; Amides

1. Introduction

Due to their similarity to many biological molecules, ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu), whose structures are shown in Fig. 1, have been used as ligands for the synthesis of coordination compounds [1,2]. On the other hand, have been shown that thermal techniques such as thermogravimetry and solution calorimetry, can be successfully employed for the study of metal–biological species interactions [3,4].

The aim of this article is to report the calorimetric study of adducts of general formula $CdCl_2{\cdot}nL$, where $n = 1$ and 2, and L = eu, etu and pu.

2. Experimental

The adducts of general formula $CdCl_2{\cdot}nL$ (where $n = 1$ and 2, and L = eu, etu and pu), were synthesized in the solid state by grinding stoichiometric amounts of the metal halide and ligand in a mortar for 70 min. A comparison of the IR spectra of free ligands and adducts, confirms that the no free ligands molecules were present after the grinding procedure. The solid state reaction procedure employed to obtain such compounds had been successful, yielding adducts with a minor amount of adsorbed water, which were dried under vacuum at room temperature for 24 h.

Carbon, nitrogen and hydrogen contents were determined using a Perkin-Elmer microelemental analyzer. The IR spectra were recorded in a Bomem apparatus in the 4000–400 cm^{-1} range, with a resolution of

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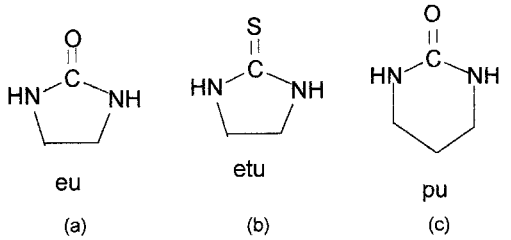

Fig. 1. Structural formulas of ethyleneurea (a); ethylenethiourea (b) and propyleneurea (c).

4 cm^{-1}. All IR spectra were obtained from powders in KBr discs.

All 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 breaking and the complete thermal effects were recorded during 300 s. Ampoules of cadmium chloride and adducts were prepared under anhydrous conditions, by using atmosphere of dry nitrogen into a dry box. 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–thioamide interactions, a complete set of thermochemical parameters were obtained. The standard molar enthalpy of reaction in condensed phase: $CdCl_2(c) + nL(c) = CdCl_2{\cdot}nL(c)$; $\Delta_r H^\theta_m$, can be calculated by using the following thermochemical cycle:

$$CdCl_2(c) + \text{solvent} = \text{Sol A}; \quad \Delta_1 H^\theta_m$$

$$\text{Sol A} + nL(c) = \text{Sol B}; \quad \Delta_2 H^\theta_m$$

$$CdCl_2 \cdot nL(c) + \text{solvent} = \text{Sol C}; \quad \Delta_3 H^\theta_m$$

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 $\Delta_4 H^\theta_m$ was obtained when ampoules of mixtures of reactants were broken into a solution of the product. So, $\Delta_r H^\theta_m$ can be calculated by Hess's law, through the equation: $\Delta_r H^\theta_m = \Delta_1 H^\theta_m + \Delta_2 H^\theta_m - \Delta_3 H^\theta_m$.

The values for the enthalpy of decomposition ($\Delta_D H^\theta_m$) and the lattice enthalpy ($\Delta_M H^\theta_m$) which corresponded to the following reactions: $CdCl_2{\cdot}nL(c) = CdCl_2(c) + nL(g)$; $CdCl_2{\cdot}nL(s) = CdCl_2(g) + nL(g)$, respectively, were calculated applying the equations: $\Delta_D H^\theta_m = -\Delta_r H^\theta_m + n\Delta^g_{cr} H^\theta_m$ (L) and $\Delta_M H^\theta_m = \Delta_D H^\theta_m + \Delta^g_{cr} H^\theta_m$ ($CdCl_2$). The acid–base enthalpy reaction in gaseous phase, $\Delta_g H^\theta_m$, which enthalpic value corresponded to $CdCl_2(g) + nL(g) = CuCl_2{\cdot}nL(g)$, can be calculated by the expression: $\Delta_g H^\theta_m = \Delta_M H^\theta_m - \Delta^g_{cr} H^\theta_m$ (L). From the $\Delta_g H^\theta_m$ values the mean metal–ligand bond dissociation enthalpy can be calculated through the expression: $D(M{-}L) = \Delta_g H^\theta_m / n$, where n is the number of ligands.

As auxiliary data for the calculations, the enthalpies of sublimation for cadmium chloride, eu and pu were used as 181.2 [4], 83.7 ± 1.9 [1] and 89.3 ± 25 [1] kJ mol^{-1}, respectively. The sublimation enthalpy of ethylenethiourea was calculated as 117.3 ± 2.1 kJ mol^{-1} by using the sublimation enthalpy value of eu, and employing an empirical equation [5] $\Delta^g_{cr} H^\theta_m$ (thioamide) $= \Delta^g_{cr} H^\theta_m$ (related amide) $\times 1.08 + 26.24$.

3. Results and discussion

The CHN elemental analysis results for the synthesized adducts, and the main infrared bands for free ligands and adducts, are summarized in Tables 1 and 2, respectively.

For cyclic amides, a decrease in the carbonyl stretching band and the increase for both, amide II and C–N stretching bands, are in agreement with a coordination through the oxygen [1,2]. For cyclic thioamides, an increase in the thioamide I, γ(C=S) $+\delta$(NCS) and γ(C−N) + δ(NCN) bands indicate that nitrogen is the donor atom [6].

Based on the previous considerations, could be verified that for eu and pu, the coordination occurs through oxygen, with exception of $CdCl_2{\cdot}2$eu, for

Table 1
Elemental analysis for adducts of general formula $CdCl_2{\cdot}nL$

Adduct	C	H	N
$CdCl_2{\cdot}$eu	13.66 (13.36)	2.22 (2.23)	10.73 (10.39)
$CdCl_2{\cdot}2$eu	20.91 (20.26)	3.38 (3.38)	16.29 (15.77)
$CdCl_2{\cdot}$etu	12.89 (12.61)	2.35 (2.10)	9.69 (9.81)
$CdCl_2{\cdot}2$etu	18.09 (18.59)	2.90 (3.10)	14.10 (14.46)
$CdCl_2{\cdot}$pu	16.80 (16.94)	2.71 (2.82)	9.59 (9.88)
$CdCl_2{\cdot}2$pu	24.89 (25.04)	4.25 (4.17)	15.01 (14.61)

Table 2
Main IR bands (cm^{-1}) for ethyleneurea, ethylenethiourea, propyleneurea and the adducts of general formula $CdCl_2{\cdot}nL$

Compound	Amide I ν(C=O)	Amide II (N–H_{def})	ν(C–N)
eu	1685	1508	1274
$CdCl_2{\cdot}$eu	1684	1515	1285
$CdCl_2{\cdot}$2eu	1686	1493	1280
pu	1690	1542	1312
$CdCl_2{\cdot}$pu	1681	1539	1314
$CdCl_2{\cdot}$2pu	1671	1542	1313
etu	1499[a]	1276[b]	1000[c]
$CdCl_2{\cdot}$etu	1522	1315	1042
CdCl2·2etu	1522	1314	1042

[a] Thioamide I.
[b] γ(C=S) + δ(NCS).
[c] γ(C–N) + δ(NCN).

which the IR are not so conclusive, whereas for etu adducts, nitrogen is the employed coordination site.

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 ±2%. All adducts releases 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. In considering adducts with the same stoichiometry, the observed thermal stability trend is: etu > pu > eu, and 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. Comparing Tables 3 and 4 data, some following conclusions could be pointed out: (1) ethyleneurea adducts are those with larger dissolution

Table 3
Dissolution enthalpy values (kJ mol^{-1}) for the dissolution steps involved in the calculation of $\Delta_r H^{\theta}_m$

Adduct	$\Delta_1 H^{\theta}_m$	$\Delta_2 H^{\theta}_m$	$\Delta_3 H^{\theta}_m$
$CdCl_2{\cdot}$eu	−17.76 ± 0.05	13.98 ± 0.02	16.25 ± 0.01
$CdCl_2{\cdot}$2eu	−17.76 ± 0.05	13.69 ± 0.01	34.50 ± 0.04
$CdCl_2{\cdot}$etu	−17.76 ± 0.05	24.27 ± 0.12	26.00 ± 0.04
$CdCl_2{\cdot}$2etu	−17.76 ± 0.05	18.34 ± 0.02	57.43 ± 0.08
$CdCl_2{\cdot}$pu	−17.76 ± 0.05	14.03 ± 0.01	9.61 ± 0.10
$CdCl_2{\cdot}$2pu	−17.76 ± 0.05	13.36 ± 0.03	12.63 ± 0.04

enthalpy, suggesting that, for those compounds, the intermolecular forces are stronger than that exhibited by eu and pu adducts. These fact are in agreement with the calculated larger lattice enthalpy values for etu adducts; (2) the D(M–L) values (Cd–O for eu and pu adducts, and Cd–N for etu ones), 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; (3) the Cd–O bond for eu adducts and Cd–N bonds for etu ones have very similar enthalpy values. This behavior is very different from that observed for eu, etu and pu copper adducts [7] for which Cu–N is ∼30 kJ mol^{-1} larger than Cu–O bonds. These fact could be in a first attempt, explained taking into account the different hardness of Cu^{2+} (borderline) and Cd^{2+} (soft); (4) ethylenethiourea adducts, which exhibits the larger decomposition enthalpy values, are indeed the most stable ones, and (5) based on the $\Delta_r H^{\theta}_m$ values, the following basicity sequence could be established: etu > eu > pu, whereas based on the Cd–L values, the sequence is etu ≡ eu > pu, showing that, in the solid state, as well as in the gaseous one, propyleneurea exhibits a weaker interaction with the metal

Table 4
Themochemical parameters (kJ mol^{-1}) for the adducts $CdCl_2{\cdot}nL$

Adduct	$-\Delta_r H^{\theta}_m$	$\Delta_D H^{\theta}_m$	$\Delta_M H^{\theta}_m$	$-\Delta_g H^{\theta}_m$	D(M–L)
$CdCl_2{\cdot}$eu	20.0 ± 01	103.7 ± 1.9	284.9	201.2	201.2
$CdCl_2{\cdot}$2eu	38.6 ± 0.1	206.0 ± 3.8	387.2	303.5	151.8
$CdCl_2{\cdot}$etu	19.9 ± 0.1	137.2 ± 2.1	318.4	201.1	201.1
$CdCl_2{\cdot}$2eu	56.9 ± 0.1	291.5 ± 2.1	472.7	310.4	155.2
$CdCl_2{\cdot}$pu	13.3 ± 0.1	102.6 ± 2.5	283.8	194.5	194.5
$CdCl_2{\cdot}$2pu	17.0 ± 0.1	195.6 ± 5.0	376.8	287.5	143.8

cation, in comparison with etu and eu. Furthermore, the $\Delta_2 H^{\theta}_{m}$ values (Table 3) suggests that also in aqueous solutions, the cadmium–etu interactions are stronger than Cd–eu and Cd–pu ones.

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