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Synthesis, characterization and thermal behavior of 18 cadmium halides adducts involving ethyleneurea, ethylenethiourea and propyleneurea

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Abstract

In this work we report on the synthesis, characterization and thermal behavior of 18 adducts of general formula $CdX_2 \cdot nL$ (where X = Cl, Br and I, $n = 1$ and 2, and L = ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu)). The IR spectroscopy results shows that for the eu and pu adducts, coordination occurs through oxygen, whereas for etu, nitrogen is used as coordination site. The thermogravimetric curves shows that the synthesized adducts releases the ligand molecules in a single mass loss step. In considering adducts with same stoichiometry, the observed thermal stability trend is etu > pu > eu.

Keywords: Cyclic amides; Cadmium halides; Adducts; Thermogravimetry

1. Introduction

Cyclic amides constitutes a particular class of compounds of great interest in coordination chemistry, due to their similarity to many biological molecules [1]. Thermochemical techniques such as thermogravimetry and solution calorimetry can be successfully used to study the interactions between metals and biological species, such as amino acids [2,3].

Many investigations dealing with the thermochemical features of adducts involving cyclic amides [4] and cyclic amides derivatives [5] have been reported, with special attention being focused on the calculation of the mean metal–ligand bond dissociation enthalpy, and the establishment of empirical equations to estimate calorimetric parameters from thermogravimetric ones [6–8].

Ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu), whose structural formulas are shown in Fig. 1, are three important cyclic amides, due to their similarities with molecules such as uracyl and biotin [1]. The eu, etu and pu, were used as models for the synthesis of copper and cobalt adducts [9] by using a solid state synthesis approach.

The aim of this publication is to report by the synthesis, characterization and thermal behavior of 18 adducts of general formula $CdX_2 \cdot nL$ (where X = Cl, Br and I, $n = 1$ and 2, and L = ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu)).

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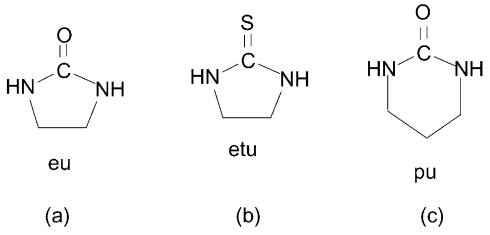

Fig. 1. Structural formulas for (a) ethyleneurea (eu), (b) ethylenethiourea (etu) and (c) propyleneurea (pu).

2. Experimental

The adducts of general formula $CdX_2{\cdot}nL$ (where X, n and L stand for the ones mentioned above), 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 ligand 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 4 cm^{-1}. The IR spectra were obtained from powders in KBr discs for all samples. Thermogravimetric (TG) curves were obtained using a Shimadzu TGA 50 apparatus under Ar atmosphere with a heating rate of 5°C min^{-1}.

3. Results and discussion

The C, H, N 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. The C, H, N contents are in good agreement with the proposed formulas.

As a general behavior 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 the fact that these ligands coordinate through the carbonyl oxygen [4,5]. For cyclic thioamides, the increase in the thioamide I, γ(C=S)+ δ(NCS) and γ(C−N) + δ(NCN) bands indicate that nitrogen is the donor atom [10].

Table 1
Elemental analysis for adducts of general formula $CdX_2{\cdot}nL$ (where X = Cl, Br and I, $n = 1$ and 2, and L = ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu))[a]

Adduct	Elemental analysis		
	C	H	N
$CdCl_2{\cdot}eu$	13.66 (13.36)	2.22 (2.23)	10.73 (10.39)
$CdCl_2{\cdot}2eu$	20.91 (20.26)	3.38 (3.38)	16.29 (15.77)
$CdBr_2{\cdot}eu$	10.14 (10.05)	1.65 (1.68)	7.58 (7.82)
$CdBr_2{\cdot}2eu$	16.21 (16.21)	2.60 (2.70)	12.41 (12.61)
$CdI_2{\cdot}eu$	8.15 (7.96)	1.56 (1.33)	5.90 (6.20)
$CdI_2{\cdot}2eu$	13.80 (13.38)	2.28 (2.23)	10.41 (10.41)
$CdCl_2{\cdot}etu$	12.89 (12.61)	2.35 (2.10)	9.69 (9.81)
$CdCl_2{\cdot}2etu$	18.09 (18.59)	2.90 (3.10)	14.10 (14.46)
$CdBr_2{\cdot}etu$	9.30 (9.62)	1.47 (1.60)	6.96 (7.48)
$CdBr_2{\cdot}2etu$	14.59 (15.12)	2.24 (2.52)	11.09 (11.76)
$CdI_2{\cdot}etu$	7.93 (7.69)	1.48 (1.28)	5.95 (5.98)
$CdI_2{\cdot}2etu$	13.45 (12.63)	2.16 (2.10)	10.21 (9.82)
$CdCl_2{\cdot}pu$	16.80 (16.94)	2.71 (2.82)	9.59 (9.88)
$CdCl_2{\cdot}2pu$	24.89 (25.04)	4.25 (4.17)	15.01 (14.61)
$CdBr_2{\cdot}pu$	12.25 (12.90)	1.98 (2.15)	6.71 (7.52)
$CdBr_2{\cdot}2pu$	20.53 (20.33)	3.33 (3.39)	11.95 (11.86)
$CdI_2{\cdot}pu$	10.73 (10.29)	1.85 (1.72)	6.21 (6.00)
$CdI_2{\cdot}pu$	16.50 (16.96)	2.77 (2.83)	9.85 (9.90)

[a] Calculated values are in parenthesis.

Based on the previous considerations, and by comparing the infrared data shown in Table 1, it could be verified that for eu and pu the coordination occurs through oxygen, with exception of $CdCl_2{\cdot}2eu$, for which the IR are not so conclusive. On the other hand, for etu adducts, nitrogen is the employed coordination site. This behavior is opposite to that exhibited by etu platinum and palladium etu compounds, for which the sulfur atom is the basic center employed [11].

The differences in electronegativity values for oxygen, nitrogen, carbon and sulfur, as verified by Pauling's scale [12], provides an explanation for the different coordination behavior observed for eu/pu and etu: O (3.44) > N (3.04) > S (2.58) > C (2.55). These differences in electronegativity promote an increased electron density on carbonyl oxygen of ethyleneurea and propyleneurea and at nitrogen atom for ethylenethiourea, as illustrated by the resonance structures previously proposed [10].

As a general trend, it can be verified that for eu and pu adducts, $\Delta\nu$(C=O) shifts, are greater for bromide

Table 2
Main IR bands (cm^{-1}) for ethyleneurea, ethylenethiourea, propyleneurea and the adducts of general formula $CdX_2{\cdot}nL$ (where X = Cl, Br and I, $n = 1$ and 2, and L = ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu))

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
$CdBr_2{\cdot}$eu	1644	1508	1275
$CdBr_2{\cdot}$2eu	1684	1506	1279
$CdI_2{\cdot}$eu	1679	1498	1277
$CdI_2{\cdot}$2eu	1677	1498	1276
pu	1690	1542	1312
$CdCl_2{\cdot}$pu	1681	1539	1314
$CdCl_2{\cdot}$2pu	1671	1542	1313
$CdBr_2{\cdot}$pu	1638	1545	1317
$CdBr_2{\cdot}$2pu	1634	1553	1315
$CdI_2{\cdot}$pu	1671	1542	1314
$CdI_2{\cdot}$2pu	1637	1542	1313
etu	1499[a]	1276[b]	1000[c]
$CdCl_2{\cdot}$etu	1522	1315	1042
$CdCl_2{\cdot}$2etu	1522	1314	1042
$CdBr_2{\cdot}$etu	1524	1273	1041
$CdBr_2{\cdot}$2etu	1522	1273	1041
$CdI_2{\cdot}$etu	1522	1311	1035
$CdI_2{\cdot}$2etu	1520	1277	1035

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

and iodine adducts, suggesting stronger metal–ligand bonds for this adducts. On the other hand, the $\Delta\nu$(C=S) shifts for etu adducts, is insensitive to the hardness of the halide.

The mass loss due to the release of ligand molecules, as calculated by using the TG curves, are in agreement with the elemental analysis results within ±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. As an illustrative example, the thermogravimetric curve for $CdBr_2{\cdot}$eu is shown in Fig. 2. The first mass loss step is due to the release of ligand molecules, and the second one is associated with the sublimation of the cadmium halide: (1) $CdX_2{\cdot}nL(s) \rightarrow CdX_2(s) + nL(g)$; (2) $CdX_2(s) \rightarrow CdX_2(g)$.

In considering adducts with the same stoichiometry, the observed thermal stability trend is etu > pu > eu.

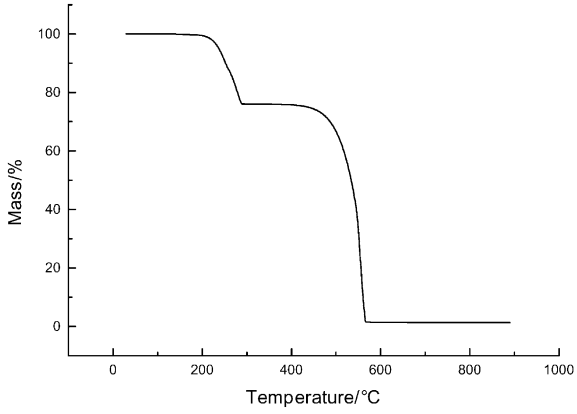

Fig. 2. Thermogravimetric curve for the adduct $CdBr_2{\cdot}$eu.

The eu, pu and etu adducts suffers thermal degradation (release of ligand molecules only) in the range 150–220, 170–220 and 220–285°C, respectively. As a general trend, bisadducts are less stable than monoadducts. For eu and pu adducts, it is observed that bromine and iodine compounds are more stable than chlorine ones, in agreement with the $\Delta\nu$(C=O) infrared shifts trends. The higher thermal stability of etu adducts in comparison with pu and eu one, was also observed for adducts of general formula $CuCl_2{\cdot}4L$ [13], and is in agreement with the calculated metal–ligand bond enthalpies, with a higher $D\langle$M–L$\rangle$ value being found for etu adduct.

Holloway and Melník [14], have reviewed crystallographic and structural data of over 600 cadmium complexes. Taking into account the structural data for cadmium compounds (one or two ligands) with molecules such as thioacetamide, urea and dimethylformamide, a polymeric structure could be supposed for the adducts studied in the present article.

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