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Solid state synthesis, characterization and thermogravimetric study of the adducts $CoCl_2 \cdot 6L$ (L = ethyleneurea, propyleneurea and ethylenethiourea)

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Abstract

The title compounds were synthesized by using an alternative solid state route, and characterized by elemental analysis, infrared spectroscopy and thermogravimetry. The IR data are in agreement with a coordination through oxygen for ethyleneurea (EU) and propyleneurea (PU) and through nitrogen for ethylenethiourea (ETU). EU, PU and ETU adducts exhibit two mass loss steps, suggesting that the coordination positions are not equivalent for all adducts, and that there are two ligand molecules closer to the metal cation. This hypothesis is supported by quantum chemical (density functional, DF) calculations. The observed thermal stability sequence is ETU > PU > EU. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cyclic amides constitutes a class of ligands of great interest in coordination chemistry, since they exhibit the active moiety –(CO)–N=, which is found in polypeptides and proteins, as well as in many other biological molecules [1].

Thermochemical techniques such as thermogravimetry and solution calorimetry, have been successfully employed to study the interactions between transition metals and biological species, such as amino acids [2,3].

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 enthalpies, 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 biological molecules such as uracyl, guanine, xanthine, thymine, cytosine, uric acid and biotin [1].

EU, ETU and PU, were recently used as ligands for the synthesis of a series of copper and cobalt adducts by using a solid state synthesis approach [9].

The aim of this publication is to report on the synthesis (by using an alternative solid state route), characterization and thermogravimetric study of the

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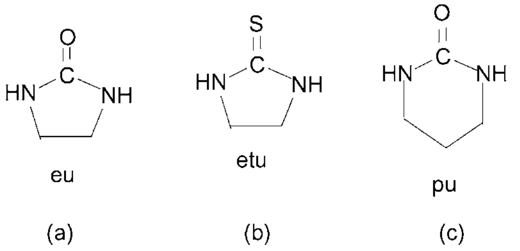

Fig. 1. Structural formulas for ethyleneurea (EU) (a), ethylenethiourea (ETU) (b) and propyleneurea (PU) (c).

adducts of general formula $CoCl_2{\cdot}6L$ (where L = EU, ETU and PU).

2. Experimental

The adducts of general formula $CoCl_2{\cdot}6L$ (where 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 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 analyser. 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}.

To calculate the metal–ligand bond lengths for the synthesized compounds, quantum chemical calculations were performed. The calculations were performed by using a density functional (DF) model, SVWN, and a DN* basis set, employing the computational package Spartan [10] version Pro 1.0.3. The calculations were performed only after a preliminary structure refinement, by using a molecular mechanics, MMFF94, minimizer.

The theoretical approach was chosen taking into account the usefulness of density functional models for theoretical studies in coordination chemistry [11]. For the $[Co{\cdot}6L]^{2+}$ systems, an octahedral geometry was assumed, taking into account that it is the most common geometry for cobalt compounds [12], even in biological systems, such as metalloproteins [13].

3. Results and discussion

The CHN elemental analysis results for the synthesized adducts, and the main IR bands for free ligands and adducts are summarized in Tables 1 and 2, respectively. As can be observed, the CHN results are in good agreement with the proposed formulas, as expected, taking into account the employed synthetic route.

As a general behavior for cyclic amides, a decrease in the carbonyl stretching band and an 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, $\gamma(C{=}S) + \delta(NCS)$ and $\gamma(C{-}N) + \delta(NCN)$ bands indicate that nitrogen is the donor atom [14].

Based on the previous considerations, and the IR data shown in Table 2, it could be verified that for EU and PU, coordination occurs through oxygen. On the other hand, for ETU adducts, nitrogen is the employed coordination site. This result for ETU adduct is opposite to what is observed for platinum and paladium ETU compounds, for which the sulphur atom is the basic coordination site employed [15].

There are some controversy about the coordination site employed by ETU: nitrogen or sulphur. In an attempt to clarify the problem, an explanation [14] based on the differences in electronegativity values for oxygen, nitrogen, carbon and sulphur, as verified by

Table 1
Elemental analysis for adducts of general formula $CoCl_2{\cdot}6L$ (where L = EU, ETU and PU)[a]

Adduct	C (%)	H (%)	N (%)
$CoCl_2{\cdot}6EU$	33.79 (33.44)	5.88 (5.57)	25.95 (26.01)
$CoCl_2{\cdot}6PU$	39.41 (39.46)	6.88 (6.58)	22.90 (23.02)
$CoCl_2{\cdot}6ETU$	29.59 (29.11)	4.96 (4.85)	22.57 (22.64)

[a] Calculated values are in parentheses.

Table 2
Main IR bands (cm^{-1}) for ethyleneurea, ethylenethiourea, propyleneurea and the adducts of general formula $CoCl_2{\cdot}6L$ (where L = EU, ETU and PU)

Compound	Amide I, ν(C=O)	Amide II, ν(N–H_{def})	ν(C–N)
Ethyleneurea	1685	1508	1274
$CoCl_2{\cdot}6EU$	1655	1508	1280
Propyleneurea	1690	1542	1312
$CoCl_2{\cdot}6PU$	1639	1544	1314
	Thioamide I	γ(C=S) + δ(NCS)	γ(C–N) + δ(NCN)
Ethylenethiourea	1499	1276	1001
$CoCl_2{\cdot}6ETU$	1519	1279	1000

Pauling's scale [16], was proposed. According to this explanation, the different coordination behaviors observed for EU, PU and ETU arise from the different electronegativity values: $O\,(3.44) > N\,(3.04) > S\,(2.58) > C\,(2.55)$. These differences in electronegativity promote an increased electron density on carbonyl oxygen of EU and at nitrogen atom for ETU, as illustrated by the resonance structures previously proposed [14]. So, for EU and PU, oxygen is the most electron-rich coordination site, whereas for ETU, this site is the nitrogen (not sulphur) atom.

The mass loss in percent due to the release of ligand molecules, as calculated by using the TG curves, are in agreement with the elemental analysis results within ±4%. As an illustrative example, the TG curve for $CoCl_2{\cdot}6ETU$ is shown in Fig. 2. EU, PU and ETU adducts exhibit two mass loss steps. The first mass loss step is associated with the release of four ligand molecules, and the second one with the release of another two. This fact strongly suggests that for all adducts, the coordination positions are not equivalent, and that there are two ligand molecules closer to the metal cation.

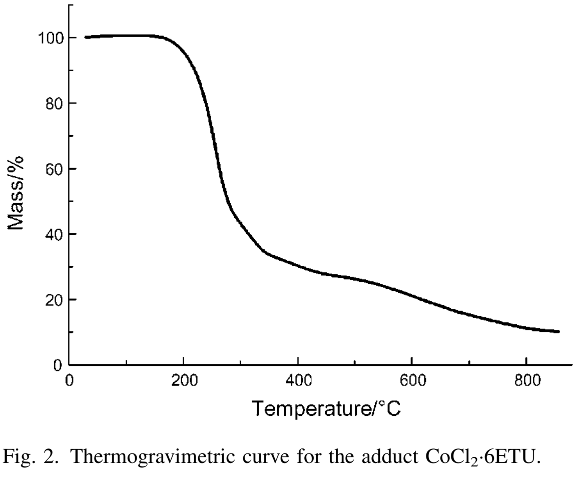

Fig. 2. Thermogravimetric curve for the adduct $CoCl_2{\cdot}6ETU$.

The proposed hypothesis about the non-equivalence of the coordination positions was reinforced by the quantum chemical calculations results. For ETU adducts, bond lengths of 263 pm were calculated for the ligands in equatorial positions, and 258 pm for the ligands in axial positions. For PU adduct, the calculated values were 199, 191, 200 and 181 pm (equatorial ligands); 184 and 202 pm (axial ligands). For EU adduct, the results are 189, 201, 179 and 207 pm (equatorial ligands); 195 and 191 pm (axial ligands). When the same quantum chemical calculations were performed for the ETU adduct, supposing a coordination through sulphur, the value of 222 pm was found for all Co–S bonds. However, such a result suggests that all ligand molecules have the same bond length, and so, will be released in a single mass loss step. This is not observed. Infrared spectroscopy, thermogravimetry and quantum chemical calculations all points to a coordination through nitrogen.

The observed thermal stability trend is ETU > PU > EU. The EU, PU and ETU adducts suffers thermal degradation (release of ligand molecules) in the range 140–240 and 240–370°C, 170–260 and 260–410°C and 180–290 and 290–670°C, respectively. The higher thermal stability of ETU adducts in comparison with PU and EU ones, was also observed for adducts of general formula $CuCl_2{\cdot}4L$, with L = EU, ETU and PU [17], and is in agreement with the calculated metal–ligand bond enthalpies, with a higher $D\langle M\text{–}L\rangle$ value being found for ETU adduct.

The longer calculated metal–ligand bond lengths for ETU adducts, suggests that the uncoordinated sulphur atom exerts a remarkable steric hindrance on the ligand molecules. On the other hand, the fact that ETU adducts are the most stable from the point of view of thermal degradation, suggests that the metal–ligand bond length (rupture of the metal–ligand bonds) is not the prominent factor for the thermal degradation of such compounds.

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