

Synthesis, characterization and a thermogravimetric study of copper, cobalt and tin mono- and bis-adducts with ethyleneurea, ethylenethiourea and propyleneurea

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Received 12 November 2001; accepted 30 November 2001

Abstract

This paper describes the synthesis, characterization and a thermogravimetric (t.g.) study of 11 adducts of general formula $MCl_2 \cdot nL$ ($M = Cu, Co$ and Sn ; $n = 1$ and 2 for Sn , and 2 for Cu and Co ; $L =$ ethyleneurea eu, ethylenethiourea etu, and propyleneurea pu). The i.r. results shows that the eu and pu adducts are coordinated through oxygen, whereas for etu nitrogen is the coordination site. The $\Delta\nu(C=O)$ or $\Delta\nu(C=S)$ trend is: $Cu > Co > Sn$. The t.g. curves show that the adducts release ligand molecules in a single mass loss step. As regards considering adducts with the same stoichiometry, the observed thermal stability trend is: $etu > pu > eu$.

Introduction

Among organic molecules, cyclic amides constitute a class of ligands of great interest in coordination chemistry, since they contain the moiety $-(CO)-N=$, which is found in macromolecules of biological interest such as polypeptides and proteins [1]. Thus, amides and thiomides can be successfully employed as models to study the possible interactions between biological species and metals. In addition, besides traditional techniques, such as i.r. spectroscopy and n.m.r., thermochemical techniques such as t.g., differential scanning calorimetry d.s.c. and solution calorimetry, have been successfully employed to study interactions between transition metals and biological species, such as amino acids [2–5].

Investigations of the thermochemical features of adducts involving cyclic amide [6] and cyclic amide derivatives [7] have been reported, 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 t.g. ones [8–14].

Ethyleneurea (eu), ethylenethiourea (etu) and propyleneurea (pu), (Figure 1) are three cyclic amides, important due to their similarities to biological molecules such as uracyl, guanine, xanthine, thymine, cytosine, uric acid and biotin [1]. Eu, etu and pu, were previously employed as ligands for the synthesis of a

series of zinc [6], cobalt [11], cadmium [12, 14] and copper [15] adducts using a solid state synthesis approach [15].

The aim of this paper is to report the synthesis, characterization and t.g. of 11 adducts of general formula $MCl_2 \cdot nL$ ($M = Cu, Co$ and Sn ; $n = 1$ and 2 for Sn , and 2 for Cu and Co ; $L =$ ethyleneurea eu, ethylenethiourea etu, and propyleneurea pu).

Experimental

The adducts $MCl_2 \cdot nL$ ($M = Cu, Co$ and Sn ; $n = 1$ and 2 for Sn , and 2 for Cu and Co ; $L =$ ethyleneurea eu, ethylenethiourea etu, and propyleneurea 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 i.r. spectra of free ligands and adducts, confirms that no free ligand molecules were present after grinding.

The solid state reaction procedure employed to obtain such compounds was successful, yielding adducts containing a minor amount of adsorbed water, which were dried under vacuum at room temperature for 24 h. The $CoCl_2 \cdot 2eu$ adduct was prepared but is very hygroscopic, and was therefore not characterized.

C, N and H contents were determined using a Perkin-Elmer microelemental analyser. I.r. spectra were recorded on a Bomem apparatus in the $4000-400\text{ cm}^{-1}$ range, with a resolution of 4 cm^{-1} . The i.r. spectra were obtained from powders in KBr discs. T.g. curves were

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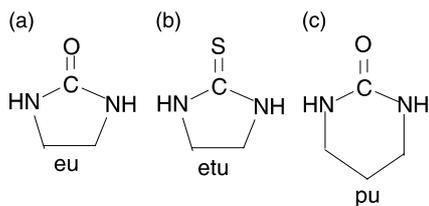


Fig. 1. Structural formulae for ethyleneurea eu (a), ethylenethiourea etu (b) and propyleneurea pu (c).

obtained using a Shimadzu TGA 50 apparatus under an Ar atmosphere at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$.

Results and discussion

The C, H and N elemental analysis results for the adducts, and the main i.r. bands for free ligands and adducts, are summarized in Tables 1 and 2, respectively. The CHN results are in good agreement with the

Table 1. Elemental analysis for adducts of general formula $\text{MCl}_2 \cdot n\text{L}$ (M = Cu, Co and Sn, $n = 1$ and 2 for Sn, and 2 for Cu and Co, and L = ethyleneurea eu, ethylenethiourea etu, and propyleneurea pu)

Adduct	Found (calcd.) %		
	C	H	N
$\text{CuCl}_2 \cdot 2\text{eu}$	23.8 (23.5)	3.5 (3.9)	18.1 (18.3)
$\text{CuCl}_2 \cdot 2\text{etu}$	21.0 (21.3)	3.3 (3.6)	16.0 (16.5)
$\text{CuCl}_2 \cdot 2\text{pu}$	28.5 (28.8)	4.7 (4.8)	16.9 (16.7)
$\text{CoCl}_2 \cdot 2\text{etu}$	21.5 (21.6)	3.6 (3.6)	16.8 (16.8)
$\text{CoCl}_2 \cdot 2\text{pu}$	29.6 (29.1)	4.9 (4.9)	16.8 (17.0)
$\text{SnCl}_2 \cdot \text{eu}$	12.9 (13.1)	2.1 (2.2)	10.3 (10.2)
$\text{SnCl}_2 \cdot 2\text{eu}$	19.5 (19.9)	3.2 (3.3)	15.9 (15.5)
$\text{SnCl}_2 \cdot \text{etu}$	12.5 (12.3)	2.1 (2.1)	8.9 (9.6)
$\text{SnCl}_2 \cdot 2\text{etu}$	18.6 (18.3)	3.0 (3.1)	13.8 (14.2)
$\text{SnCl}_2 \cdot \text{pu}$	16.30 (16.6)	2.7 (2.8)	9.2 (9.7)
$\text{SnCl}_2 \cdot 2\text{pu}$	24.7 (24.6)	4.0 (4.1)	14.9 (14.4)

Table 2. Main i.r. bands (cm^{-1}) for eu, etu, pu and adducts of general formula $\text{MCl}_2 \cdot n\text{L}$ (M = Cu, Co and Sn, $n = 1$ and 2 for Sn, and 2 for Cu and Co, and L = eu, etu and pu)

Compound	amide I $\nu(\text{C}=\text{O})$	amide II ($\text{N}-\text{H}_{\text{def}}$)	$\nu(\text{C}-\text{N})$
eu	1685	1508	1274
$\text{CuCl}_2 \cdot 2\text{eu}$	1645	1526	1285
$\text{SnCl}_2 \cdot \text{eu}$	1637	1508	1283
$\text{SnCl}_2 \cdot 2\text{eu}$	1674	1504	1279
pu	1690	1542	1312
$\text{CuCl}_2 \cdot 2\text{pu}$	1625	1573	1317
$\text{CoCl}_2 \cdot 2\text{pu}$	1638	1548	1316
$\text{SnCl}_2 \cdot \text{pu}$	1639	1618	1319
$\text{SnCl}_2 \cdot 2\text{pu}$	1639	1618	1317
etu	1499 ^a	1276 ^b	1000 ^c
$\text{CuCl}_2 \cdot 2\text{etu}$	1538	1283	1028
$\text{CoCl}_2 \cdot 2\text{etu}$	1530	1280	1038
$\text{SnCl}_2 \cdot \text{etu}$	1517	1356	1017
$\text{SnCl}_2 \cdot 2\text{etu}$	1514	1375	1041

^a Thioamide I; ^b $\gamma(\text{C}=\text{S}) + \delta(\text{NCS})$; ^c $\gamma(\text{C}-\text{N}) + \delta(\text{NCN})$.

proposed formulae, as expected, taking into account the synthetic route employed.

As is generally observed for cyclic amides, a decrease in the carbonyl stretching band and increases for both, amide II and C–N stretching bands, are in agreement with the fact that these ligands coordinate through the carbonyl oxygen [6, 7]. For cyclic thioamides, the increase in the thioamide I, $\gamma(\text{C}=\text{S}) + \delta(\text{NCS})$ and $\gamma(\text{C}-\text{N}) + \delta(\text{NCN})$ bands indicate that nitrogen is the donor atom [16].

Based on previous considerations, and comparing the i.r. data shown in Table 2, we verify that for eu and pu, coordination occurs through oxygen. On the other hand, for etu adducts, nitrogen is the coordination site. This behaviour contrasts with that for platinum and palladium etu compounds, for which the sulphur atom is the basic centre [17].

The differences in electronegativity values for oxygen, nitrogen, carbon and sulphur, according to Pauling's scale [18], provides an explanation for the different coordination behaviour observed for eu/pu and etu: O (3.44) > N (3.04) > S (2.58) > C (2.55). These differences in electronegativity promote an increase in the electron density on the carbonyl oxygen of ethyleneurea and propyleneurea and on the nitrogen atom for ethylenethiourea, as illustrated by the resonance structures previously proposed [16].

It can be verified that $\Delta\nu(\text{C}=\text{O})$ or $\Delta\nu(\text{C}=\text{S})$ follows the sequence: Cu > Co > Sn, suggesting that the metal–ligand bond strength could follow the same trend.

The mass loss percentages due to the release of ligand molecules, calculated using the t.g. curves, are in agreement with the elemental analysis results in the $\pm 3\%$ range. All adducts release ligand molecules in a single mass loss step, suggesting that, in the bisadducts, both ligand molecules occupy equivalent coordination sites, exhibiting similar bond enthalpies. As an illustrative example, the t.g. curve for $\text{CuCl}_2 \cdot 2\text{eu}$ is shown in Figure 2.

In considering adducts with the same stoichiometry, the observed thermal stability trend is: etu > pu > eu. The eu, pu and etu adducts suffer thermal degradation

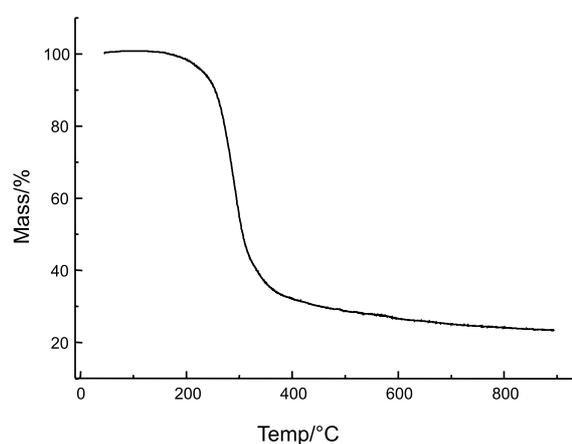


Fig. 2. T.g. curve for the $\text{CuCl}_2 \cdot 2\text{eu}$ adduct.

(release of ligand molecules) in the 170–400, 180–380 and 205–470 °C range, respectively. The higher thermal stability of the etu adducts in comparison with pu and eu adducts, was also observed for adducts of general formula $\text{CuCl}_2 \cdot 4\text{L}$, L = eu, etu and pu [19], and is in agreement with the calculated metal–ligand bond enthalpies, a higher $D\langle\text{M-L}\rangle$ value being found for the etu adduct.

For tin adducts, it is verified that *bis*adducts are less stable than monoadducts, which suggests higher metal–ligand bond enthalpy values for the latter.

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TMCH 5244