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Adducts of cyclic ureas with zinc halides – a thermochemical study

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Abstract

Adducts formed between ZnX_2 ($X = Cl$, Br, I) and 2-imidazolidinone (ethyleneurea, EU) or tetrahydro-2-pyrimidone (propyleneurea, PU) of the general formula $ZnX_2{\cdot}2L$ ($L = Eu$ or PU) had the standard molar enthalpies determined through reaction-solution calorimetry at 298.15 K: $ZnX_2(cr) + 2L(cr) = ZnX_2{\cdot}2L\ (cr)$; $\Delta_r H_m^0/kJ\ mol^{-1}$: $ZnX_2{\cdot}2EU$, $-(46.04 \pm 0.72)$; $-(45.35 \pm 0.58)$ and $-(59.20 \pm 0.83)$ for chloride, and iodide, and $ZnX_2{\cdot}2PU$, $-(44.26 \pm 2.63)$; $-(37.75 \pm 1.83)$ and $-(46.96 \pm 1.43)$ for the same sequence of halides. From these values, the standard molar enthalpies of the crystalline adducts were calculated for both the series. The standard molar enthalpies of sublimation for EU and PU were calculated by means of differential scanning calorimetry to give 83.7 ± 1.9 and $89.3 \pm 2.5\ kJ\ mol^{-1}$, respectively. These values enabled the calculation of the corresponding standard molar enthalpies of adducts in the gaseous phase. From these latter enthalpic values, the mean zinc-oxygen bond enthalpies were determined as 139.4 ± 2.2, 130.1 ± 2.2, 131.4 ± 2.2 and 141.3 ± 3.2, 129.1 ± 3.0, $128.2 \pm 3.0\ kJ\ mol^{-1}$ for EU and PU adducts, for the above sequence of halides.

Keywords: Zinc halides; Propyleneurea; Ethyleneurea; Thermochemistry

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1. Introduction

The most common cyclo-urea derivatives are formed by two or three methylene groups bonding both, the nitrogen atoms of the precursor urea, corresponding to 2-imidazolidinone, and tetrahydro-2-pyrimidone. Both these crystalline neutral, colourless and odourless solids are also designated as ethyleneurea (EU) (Fig. 1(a)) and propyleneurea (PU) (Fig. 1(c)). The methylation of the first compound can cause a strong change in physical properties, while transforming it to a liquid at room temperature (Fig. 1(b)), which has been used as solvent for spectroscopic studies or synthesis [1,2].

From the point of view of coordination chemistry, this kind of molecules has potentially both, nitrogen and also the oxygen atoms available to bond to an acid centre. In spite of the great ease in finding these as pure compounds, its coordination chemistry deals with a relatively low volume of data. However, the oxygen atom proved to be the basic centre used to coordinate the metal in forming adducts. This statement is illustrated by adducts formed between ethyleneurea with zinc(II), cadmium(II), copper(II), iron(III) and cobalt(III) chlorides [3]. In this series of compounds, zinc and iron showed the maximum decrease in carbonyl

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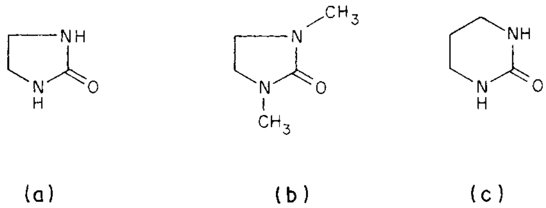

Fig. 1. Structural forms of ethyleneurea (a) *N,N'*-dimethylethyleneurea (b) and propyleneurea (c).

stretching frequency. This has been taken as a clear indication of the effective metal–ligand bond formation.

Adducts of tin or titanium(IV) halides [4] were explored with ethyleneurea and the metal is coordinated through ligand by carbonyl oxygen atom. For these adducts, the basic character of the halides decreases in the following order: Cl > Br > I. This sequence was established by considering the progressive decrease in CO stretching frequency of the adducts formed. However, adducts involving the methylated ligands, such as dimethylethyleneurea and dimethylpropyleneurea, with cobalt(II) halides [5] showed some controversy in the assignment of CO and CN stretching frequencies. It was supposed that the apparent opposite shift of these bands resulted in a certain overlap causing the infrared spectra to show only a single band [5].

It is worth mentioning that ethylene- and propyleneurea molecules are structurally similar to many important biological polypeptides and proteins. The elucidation of their chemical and physical properties can be very useful to an understanding of peptidic bonds [6]. On the other hand, zinc–oxygen bond formation has an important role from the biological point of view, because the replication of DNA molecules is dependent on it [7] and the enthalpic determination can illustrate the importance of the energetics involved in this biological process.

In the course of the development of coordination chemistry, the structural features were always thoroughly explored. However, a lack of thermochemical study for adducts of this kind of system is clearly rare. Thus, the main purpose of this report is to acquire information on the adducts of zinc halides with ethylene- and propyleneureas. In this context, these series of halides have been previously studied with dimethylethyleneurea (DMEU) [8]. The isolated adducts $ZnX_2 \cdot 2DMEU$ (X = Cl, Br or I) showed a decrease in CO stretching frequency due to the metal–oxygen bond formation. The thermochemical data previously obtained for this system will be joined to establish some correlations with the adducts $ZnX_2 \cdot 2L$ (L = Cl, Br, I and L = EU, PU) reported here.

2. Experimental

The anhydrous metal halides were prepared in the laboratory or purified from commercial products (Merck or Carlo Erba). Ethanol and diethylether used in all preparations were distilled and kept dry. The reagent grade ethyleneurea and propyleneurea (Aldrich) were used without further purification. Ethanol for calorimetric determinations was refluxed over calcium oxide, distilled, refluxed over magnesium and iodine, and then fractionally distilled.

All adducts were obtained by using the same procedure as described previously [8]. Briefly, the ligand was dissolved in diethylether or ethanol and was added dropwise to the solution of a given halide dissolved in the same solvent. In all the cases, the ligand : metal molar proportion was larger than 1 : 4. A white solid started to form immediately and the reaction was complete in 1 h. The solid was filtered, washed with diethylether, dried under vacuum for 24 h and maintained under dry atmosphere in a desiccator. The degree of metal in each adduct was determined by EDTA titration and halides by potentiometric silver nitrate titration as described earlier [9,10]. Infrared spectra in the 400–4000 $\mathrm{cm^{-1}}$ range were obtained with a Perkin–Elmer 1320 instrument using Nujol mulls.

The enthalpy of fusion and heat capacities of both the ligands in solid and liquid forms were obtained in DuPont model 910 differential scanning calorimeter (DSC), purged with dry argon, using a programmed heating rate of 0.083 $\mathrm{K\,s^{-1}}$. The reaction-solution calorimetric measurements were performed in an isoperibolic calorimetric system [8] as already described. Ampoules containing 10–60 mg of metal halides, ligands or adducts were prepared in a dry box and broken into a glass reaction vessel, charged with 0.10 $\mathrm{dm^3}$ of suitable calorimetric solvent at 298.15 ± 0.20 K.

3. Results and discussion

All adducts are white and non-hygroscopic. The ligands used, 2-imidazolidinone or tetrahydro-2-pyrimidone, have been also designated here as ethyleneurea (EU) and propyleneurea (PU), respectively. In all preparations, the excess of ligands force the synthesis of adducts with the same stoichiometry. The elemental analyses results are in good agreement with the set of the proposed general formula for adducts as $ZnX_2{\cdot}2L$ ($X = Cl$, Br, I and $L = EU$, PU). The infrared spectra for the adducts with EU or PU were very similar, showing absorption bands very close to that of the free ligand. Nevertheless, CO and CN stretching frequencies are more sensitive after metal-coordination. As expected, a decrease and an increase in frequencies of $\sim$20 and $\sim$10 cm^{-1}, respectively, were observed for both the frequencies. This is a normal behaviour found for this kind of ligands, corroborating the metal-ligand bond occurring through the oxygen donor atom of the carbonyl group [11–18].

Taking into account the mode of coordination, the effort is made to get information about zinc–oxygen bond in these adducts. In this connection, the standard molar enthalpies $\Delta_r H_m^0$ of the adducts $ZnX_2{\cdot}2L$ were determined at the temperature 298.15 K based on the general thermochemical reaction:

$$ZnX_2(cr) + 2L(cr) = ZnX_2 \cdot nL(cr).$$

The standard molar enthalpy $\Delta_r H_m^0$ of this reaction was obtained by measuring the enthalpy of dissolution of reactants and products into a suitable calorimetric solvent. In the first stage, the anhydrous metal halide was dissolved in ethanol, followed by dissolution of the stoichiometric amount of ligand. In an independent operation, the adduct was also dissolved in ethanol. In each step, the individual enthalpic value is collected as represented by the following sequence of reactions:

$$ZnX_2(cr) + \text{ethanol} = \text{Solution A} \quad \Delta_1 H_m^0$$

$$2L(cr) + \text{Solution A} = \text{Solution B} \quad \Delta_2 H_m^0$$

$$ZnX_2 \cdot 2L(cr) + \text{ethanol} = \text{Solution C} \quad \Delta_3 H_m^0$$

$$\text{Solution B} = \text{Solution C} \quad \Delta_4 H_m^0$$

A strict control of the stoichiometries in each step of the calorimetric reactions was used to produce the dissolution of reactants in the successive steps, in order to obtain the same composition as those of the products. From the sequence of dissolutions listed in Table 1, values of $\Delta_r H_m^0$ were obtained by applying

Table 1
Standard molar enthalpies of dissolution $\Delta_{sol} H_m^0$ (kJ mol^{-1}) in ethanol (EtOH) at 298.15 K. The number of experiments in each case was five

	Reagent	Solvent	Solution	$\Delta_{sol} H_m^0$
1	$ZnCl_2$ (cr)	EtOH	A_1	−43.10 ± 0.60
2	2EU (cr)	A_1	A_2	37.56 ± 0.29
3	$ZnCl_2{\cdot}2EU(cr)$	EtOH	A_3	40.50 ± 0.26
4	$ZnBr_2(cr)$	EtOH	B_1	−47.50 ± 0.26
5	2EU(cr)	B_1	B_2	37.83 ± 0.25
6	$ZnBr_2{\cdot}2EU(cr)$	EtOH	B_3	35.49 ± 0.37
7	$Znl_2(cr)$	EtOH	C_1	−52.88 ± 0.35
8	2EU(cr)	C_1	C_2	38.08 ± 0.39
9	$Znl_2{\cdot}2EU(cr)$	EtOH	C_3	34.49 ± 0.65
10	$ZnCl_2(cr)$	EtOH	D_1	−43.10 ± 0.60
11	2PU(cr)	D_1	D_2	37.33 ± 2.50
12	$ZnCl_2{\cdot}2PU(cr)$	EtOH	D_3	38.49 ± 1.20
13	$ZnBr_2$ (cr)	EtOH	E_1	−47.50 ± 0.26
14	2PU(cr)	E_1	E_2	49.09 ± 0.65
15	$ZnBr_2{\cdot}2PU(cr)$	EtOH	E_3	39.15 ± 1.67
16	Znl_2 (cr)	EtOH	F_1	−52.88 ± 0.35
17	2PU(cr)	F_1	F_2	49.06 ± 0.39
18	$Znl_2{\cdot}2PU(cr)$	EtOH	F_3	43.14 ± 1.33

Table 2
Summary of the thermochemical results (kJ mol^{-1})

Adduct	$\Delta_r H_m^0$	$\Delta_D H_m^0$	$\Delta_M H_m^0$	$\Delta_g H_m^0$	$\langle D\rangle$(M–O)
$ZnCl_2 \cdot 2EU$	-46.04 ± 0.72	213.4 ± 3.9	362.4 ± 4.0	278.7 ± 4.4	139.4 ± 2.2
$ZnBr_2 \cdot 2EU$	-45.35 ± 0.58	212.8 ± 3.8	343.8 ± 3.9	260.1 ± 4.3	130.1 ± 2.2
$ZnI_2 \cdot 2EU$	-59.20 ± 0.83	226.6 ± 3.9	346.6 ± 4.0	262.7 ± 4.4	131.4 ± 2.2
$ZnCl_2 \cdot 2PU$	-44.26 ± 2.65	222.9 ± 5.7	371.9 ± 5.8	282.6 ± 6.3	141.3 ± 3.2
$ZnBr_2 \cdot 2PU$	-37.75 ± 1.83	216.4 ± 5.3	347.7 ± 5.4	258.1 ± 6.0	129.1 ± 3.0
$ZnI_2 \cdot 2PU$	-46.96 ± 1.43	225.6 ± 5.2	345.6 ± 5.3	256.3 ± 5.9	128.2 ± 3.0
$ZnCl_2 \cdot 2DMEU$ [a]	-67.31 ± 0.76	187.4 ± 2.1	336.4 ± 2.3	276.4 ± 2.7	138.2 ± 1.4
$ZnBr_2 \cdot 2DMEU$ [a]	-84.70 ± 2.19	203.8 ± 2.3	334.8 ± 2.5	274.8 ± 2.9	137.4 ± 1.5

[a] Ref. [8].

the foregoing thermochemical cycle. A null enthalpy $\Delta_4 H_m^0$ was obtained when ampoules of mixtures of reactants were broken into a solution of the product. Thereafter, the enthalpy of the acid–base interaction in the condensed phase can be calculated by means of the expression: $\Delta_r H_m^0 = \Delta_1 H_m^0 + \Delta_2 H_m^0 - \Delta_3 H_m^0$, whose values are listed in Table 2.

From $\Delta_r H_m^0$ values, the enthalpies of the reactions given below, can be calculated:

$$ZnX_2 \cdot 2L(cr) = ZnX_2(cr) + 2L(g)$$

$$ZnX_2 \cdot 2L(cr) = ZnX_2(g) + 2L(g)$$

For both these equations, the following expression can be derived:

$$\Delta_D H_m^0 = -\Delta_r H_m^0 + 2\Delta_{cr}^{g} H_m^0(\mathrm{L})$$

$$\Delta_M H_m^0 = -\Delta_D H_m^0 + 2\Delta_{cr}^{g} H_m^0(\mathrm{ZnX_2})$$

In the last expression $\Delta_{cr}^{g} H_m^0$ values used were 149.0 ± 1.0; 131.0 ± 1.0 and 120.0 ± 1.0 kJ mol^{-1} ZnX_2 (X=Cl, Br, I), respectively [19,20].

Table 3
Heat capacities (kJ mol^{-1}) and standard molar enthalpies (kJ mol^{-1}) for ethyleneurea (EU) and propyleneurea (PU)

	EU	PU
C_p(cr)	0.13 ± 0.01	0.20 ± 0.01
C_p(l)	0.15 ± 0.04	0.17 ± 0.02
C_p(g)	0.10 ± 0.01	0.14 ± 0.02
$\Delta_{cr}^{l} H_m^0 (T_{fus})$	14.7 ± 1.2	30.6 ± 1.9
$\Delta_{l}^{g} H_m^0\ (T_{vap})$	63.4 ± 1.5	44.4 ± 1.7
$\Delta_{cr}^{g} H_m^0$	83.7 ± 1.9	89.3 ± 2.5

The standard enthalpies of sublimation of both the ligands were determined by means of the DSC technique and estimation methods. Both the curves showed one sharp peak, which is attributed to the fusion at 403 and 523 K, for EU and PU, respectively. A corresponding broad peak at 453 and 553 K was assigned to the vaporization process. Using the values of $\Delta_{cr}^{l} H_m^0$ (T_{fus}) and $\Delta_{l}^{g} H_m^0$ (T_{vap}) and the heat capacities of the solid and liquid ligands as obtained by DSC [21], and the gaseous heat capacity as determined using the method of generalized vibrational assignment [22], the standard molar enthalpies of sublimation were estimated for both the ligands. The gaseous phase heat capacities have the following forms: $C_p(g) = 7.01 \times 10^{-3} + 3.73 \times 10^{-4} T - 1.93 \times 10^{-1} T^2$ for EU and $C_p(g) = -7.83 \times 10^{-3} + 5.73 \times 10^{-4} T - 2.66 \times 10^{-7} T^2$ for PU. All these quantities are listed in Table 3. From these data, the standard enthalpies of sublimation were calculated for both the ligands by applying the tabulated data in the expression:

$$\Delta_{cr}^{g} H_m^0(298\,\mathrm{K}) = \int_{298}^{T_{fus}} C_p(\mathrm{cr})\mathrm{d}T + \Delta_{cr}^{l} H_m^0(T_{fus}) + \int_{T_{fus}}^{T_{vap}} C_p(l)\mathrm{d}T + \Delta_{l}^{g} H_m^0(T_{vap}) - \int_{298}^{T_{vap}} C_p(\mathrm{g})\mathrm{d}T$$

The calculated values gave 83.7 ± 1.9 and 89.3 ± 2.5 kJ mol^{-1} for EU and PU, respectively.

The enthalpy related to the mean metal–ligand bond in the gaseous phase, $\Delta_g H_m^0$, can be calculated from $\Delta_M H_m^0$ by means of the expression:

$\Delta_g H_m^0 = \Delta_M H_m^0 - \Delta_s H_m^0$, where the last value is the enthalpy of sublimation of the adduct in the following equation:

$$ZnX_2 \cdot 2L(g) = ZnX_2(g) + 2L(g)$$

As the infrared spectroscopy indicated that the metal is monocoordinated by the ligand through the oxygen atom, the mean metal–oxygen bond enthalpy can be calculated from $\langle D \rangle(M\text{–}O) = \Delta_g H_m^0/2$. However, the adducts decompose on heating and the respective enthalpy is not experimentally accessible. Based on a series of sublimable adducts, the established hypothesis permitted to establish that $\Delta_s H_m^0 = \Delta_{cr}^{g} H_m^0(L)$ [23]. From this assumption, the enthalpy of the reaction in the gaseous phase can be calculated and, consequently, the mean enthalpy of the metal–oxygen bond obtained. These values are listed in Table 2. A comparison of these values is favourable due to the fact that all them have the same stoichiometry. Thus, for both the series of zinc adducts, $\langle D \rangle(M\text{–}O)$ values are 139.4 ± 2.2 and 141.3 ± 3.2 kJ mol^{-1}, for zinc chloride with EU and PU. These values are higher in comparison to bromide and iodide, which gave very close values of 130.1 ± 2.2, 131.4 ± 2.2 and 129.1 ± 3.0, 128.2 ± 3.0 kJ mol^{-1} for the same sequence of ligands.

The ligand dimethylethyleneurea (DMEU) forms adducts with zinc chloride and bromide with the same stoichiometries as those described here. The thermochemical results for these adducts are also included in Table 2 for comparison. Thus, the mean metal–oxygen bond enthalpies are close to these tabulated values, being 138.2 ± 1.4 and 137.4 ± 1.5 kJ mol^{-1}, respectively [8]. In examining these enthalpy values, it seems that the inductive effect caused by the methyl group on the molecule of the ligand did not reflect in an increase of the effectiveness of the bond on metal.

Although the adducts involving DMEU are restricted to zinc chloride and bromide, as shown in Table 2, the values of $\Delta_r H_m^0$ reflect the inductive effect in the molecule [24,25]. By considering any of these halides as a standard acid, the order of basicity can be established as DMEU > EU > PU, as a consequence of the hardness of the oxygen atom in these cyclic ureas, caused by the increased electronic density around the oxygen atom in the DMEU molecule.

The mean metal–oxygen bond enthalpies obtained here for $ZnCl_2 \cdot 2L$ have comparable values with some other adducts of the same stoichiometries, involving a series of oxo-ligand like phosphine oxides [26–28], urea [29] and derivatives [30–32], amides [33–35] and pyridine oxide [36]. For these ligands $\langle D \rangle(M\text{–}O)$ was systematized to have a mean value of 146 ± 10 kJ mol^{-1}. So, the present obtained values are within the established general behaviour. A better comparison should be done by considering the previous reported values involving urea and derivatives as methyl-, *N*,*N*'-dimethyl and tetramethylureas. In particular, tetramethylurea presented a complete set of data for halides in the sequence 148, 139, 145 and 142, 135, 149 kJ mol^{-1} for chloride, bromide and iodide, respectively. The highest separation observed with the present series of data occurred with zinc iodide values, even though it is not well expressed. On the other hand, in examining the structure of ligands, it is noticed that the substituted bulk urea molecules contain two (EU) or three (PU) methylene groups bonded to both the urea nitrogen atoms in forming cycles. Apparently, this structural arrangement did not disturb the coordination as could be expected for the possible steric effect which, in principle, could affect these ligands in the mean metal–oxygen bond enthalpy in these series of adducts.

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