Thermochimica Acta, 125 (1988) 295–305
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOCHEMICAL STUDY OF ADDUCTS OF UREA WITH ZINC, CADMIUM AND MERCURY: SOME CORRELATIONS FOR UREA DERIVATIVES

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(Received 8 June 1987)

ABSTRACT

The adducts $ZnX_2 \cdot 2ur$ (X = Cl, Br, I), $CdX_2 \cdot 2ur$ (X = Br, I), $CdX_2 \cdot ur$ (X = Cl, Br, I) and $HgX_2 \cdot ur$ (X = Cl, Br) have been characterized. The shifts of the stretching vibrations to low frequency (νCO) and to high frequencies (νCN and νNH) indicated that urea (ur) is oxygen-bonded to the metals. The standard molar enthalpies for the reaction $MX_2(c) + n\,ur(c) = MX_2 \cdot n\,ur(c)$ $\Delta_r H_m^\ominus$ were determined by solution-reaction calorimetry, given the following values: $ZnCl_2 \cdot 2ur(c)$, -59.72 ± 0.30; $ZnBr_2 \cdot 2ur$, -59.41 ± 0.89; $ZnI_2 \cdot 2ur$, -81.74 ± 0.89; $CdCl_2 \cdot ur$, -21.54 ± 0.18; $CdBr_2 \cdot ur$, -13.88 ± 0.28; $CdI_2 \cdot ur$, -30.75 ± 0.36; $CdBr_2 \cdot 2ur$, -24.40 ± 0.21; $CdI_2 \cdot 2ur$, -19.69 ± 0.17; $HgCl_2 \cdot ur$, -9.39 ± 0.13 and $HgBr_2 \cdot ur$, $+1.00 \pm 0.78$ kJ mol^{-1}. From these values, the standard molar enthalpies of formation ($\Delta_f H_m^\ominus$) and of decomposition ($\Delta_D H_m^\ominus$), and lattice enthalpy ($\Delta_M H_m^\ominus$) were calculated and the mean molar enthalpy of the metal–oxygen bond [$\bar{D}$(M–O)] was estimated. The thermochemical results indicate a decrease in stability of the adducts from zinc to mercury. The degree of hydrogen bonding affects differently the enthalpies of formation of adducts in solid state for urea and its derivatives.

INTRODUCTION

The planar structure of the urea (ur) molecule [1] favours its interaction with metals, through the oxygen or nitrogen atoms [2], and induces a high degree of self association through hydrogen bonding [3–5]. This property has been used in a direct competition with the amide groups of the peptide chains of proteins. The action of urea in these folded structures produces a random coil conformation of the protein, and consequently is extensively used in the study of biological reactions [6,7].

From the point of view of co-ordination chemistry, urea ranks foremost. The first review of oxo-compound adducts [8] mentioned the complexes $ZnCl_2 \cdot 2ur$, $CdCl_2 \cdot 2ur$ and $CuCl_2 \cdot ur$, which were prepared in 1857 [9].

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0040-6031/88/$03.50

Various techniques were employed to establish the main structural characteristics of the free molecule, including one of the first X-ray determinations of an organic compound [10]. Subsequent determinations have confirmed the planarity of the molecule and that this structural feature is maintained in complexes [10–13].

Extensive studies of urea, which has the ability to form complexes using the oxygen or nitrogen as basic centre, have concluded that the mode of interaction depends on the characteristics of the metals [14]. Thus the soft acids, like palladium or platinum, prefer the nitrogen on co-ordination [2]. Divalent cations (hard acids) are directed to the oxygen as the site of co-ordination with no dependence between the C=O–M angle and the O–M distance [13].

This study deals with the zinc group halides and their urea adducts. Although some of these adducts have been known since the last century, studies of these compounds were renewed only in the fifties, mainly due to the interest in their structural features. Since then, the structures of many adducts have been determined [11–13,15,16].

In our study, the $ZnX_2 \cdot 2ur$ (X = Cl, Br, I), $CdX_2 \cdot 2ur$ (X = Br, I), $CdCl_2 \cdot ur$ and $HgX_2 \cdot ur$ (X = Cl, Br) adducts were isolated and characterized with the main objective focused on the thermochemical data for this series of compounds.

The thermochemical results obtained for the urea derivatives, tetramethylurea (tmu) [17], *N*,*N*′-dimethylurea (dmu) [18] and methylurea (mu) [19], showed the decrease in basicity tmu > dmu > mu, which follows the inductive effect of the methyl groups with the successive replacement of the hydrogens on the nitrogen atoms of urea [19]. On the other hand, the following correlation (with an error of less than 1%) was obtained from the enthalpies of combustion: $\Delta_c U^\ominus$ (ureas)/kJ $\mathrm{mol}^{-1} = -49.14\,M + 2305.15$, where M is the molar mass of the urea or its derivative [19].

These thermochemical data can contribute to understanding the energetics of bonding formation in more complex systems. To illustrate this point, one remembers that the replication of DNA molecules by DNA polymerase depends on the formation of zinc–oxygen bonds [20]. Amongst other parameters, this publication reports mean metal–oxygen bond ethalpies including the zinc–oxygen bond.

EXPERIMENTAL

Reagents

Urea (Fisher) was recrystallized in anhydrous enthanol at −5 °C and dried for several hours in vacuo. Halides of zinc, cadmium and mercury, prepared or reagents grade, were dried before use [17]. Ethanol and methanol

TABLE 1

Metal elemental analyses, melting point, and infrared bands (cm^{-1})

Substance	M (%) [a]	M.P. (°C)	νN–H	νCO	νCN
$ZnCl_2 \cdot 2ur$	25.50 (25.6)	125–126	3445, 3340, 3240	1630	1480
$ZnBr_2 \cdot 2ur$	18.91 (18.9)	122–123	3450, 3345, 3245	1642	1490
$ZnI_2 \cdot 2ur$	14.91 (14.8)	135–137	3450, 3340	1630	1485
$CdCl_2 \cdot ur$	46.19 (45.9)	> 230	3475, 3375, 3220	1635	1475
$CdBr_2 \cdot ur$	33.83 (33.9)	> 230	3467, 3360, 3200	1630	1460
$CdI_2 \cdot ur$	26.36 (26.2)	165–166	3450, 3360	1625	1485
$CdBr_2 \cdot 2ur$	28.65 (28.3)	119–120	3475, 3365	1630	1475
$CdI_2 \cdot 2ur$	23.11 (23.2)	126–127	3445, 3340, 3245	1660	1465
$HgCl_2 \cdot ur$	60.50 (60.4)	198–202	3445, 3340, 3250	1640	1485
$HgBr_2 \cdot ur$	47.71 (47.5)	202–205	3450, 3337	1635	1480
ur	–	135	3340, 3330, 3245	1680	1450

[a] Values found are given in parentheses.

were treated with calcium oxide for a long period and then distilled. Ether was previously dried over calcium chloride for 24 h, distilled over metallic sodium and redistilled. All solvents were stored over molecular sieves. The air-sensitive halides and adducts were handled in a dry-box during the preparation of the ampules used in the calorimetric measurements.

Preparation of the adducts

All operations involved in the preparation and purification were carried out either in vacuo or in a dry-box under an atmosphere of dried nitrogen.

The preparation procedure is basically the same for all adducts [12]. With the exception of $CdBr_2 \cdot 2ur$ and mercury halides adducts, where the metal halide : ligand ratios were 1 : 4 and 1 : 5, respectively, all other preparations were performed by the addition of an ethanolic solution of urea, with the stoichiometry indicated in Table 1, to a stirred solution of metal halide dissolved in ethanol. The solution was stirred for 2 h and, after part of the solvent was evaporated at reduced pressure, crystals appeared slowly. The solid was filtered, washed with cold ether and dried in vacuo. The mercury adducts were isolated only after maintaining the solution at −5 °C for several hours. The yield in these preparations vary from 60 to 90%. Attempts to isolate adducts with other stoichiometry were unsuccessful.

Analysis of the complexes

Good agreement with the proposed stoichiometry was obtained by the metal elemental analysis through spectrophotometric titration with EDTA [19].

Calorimetric measurements

All calorimetric determinations were performed in an LKB 8700 precision reaction solution calorimeter at 298.15 ± 0.02 K. The sample (5 to 100 mg), sealed in a thin glass ampule, was broken in 100.0 cm^3 of calorimetric solvent. Details of the measurement procedure, the apparatus, and data processing have been previously described [21]. Ethanol, methanol and ethanol–2 M HCl were used as calorimetric solvent because of their capacities to dissolve ligand, halides and adducts.

Other measurements

Infrared spectra, thermogravimetric curves, melting points, and mass spectra were obtained as before [22].

RESULTS

All adducts are white solids. The hygroscopicity and solubility in ethanol decrease from zinc to mercury, the iodides being the most soluble among the halides. The metal analyses, melting points, and the main infrared bands are summarized in Table 1. The melting points are not reproducible because of the decomposition of these complexes during heating. The thermogravimetric curves of $CdX_2 \cdot ur$ ($X = Cl, Br$) and $CdI_2 \cdot 2ur$ showed loss of mass below the melting points, which characterizes a real interval of decomposition [22].

The total mass loss showed by the thermogravimetric curves confirmed the stoichiometry proposed for the adducts. The compounds $ZnX_2 \cdot 2ur$ ($X = Cl, Br, I$) lose the ligands in a first step, followed by the sublimation of the metal halides. However, a residue (21%) remains for the chloride, which seems to be a general behaviour for all zinc chloride adducts. The mono-adducts of cadmium lose the ligands followed by the sublimation of metal halides, but a high residue (21%) was observed for iodide. Nevertheless, the bis-adducts behave like the zinc adducts and a residue (6.6%) was also detected for the iodide complex. Both adducts of mercury totally lost the mass in a single step. This indefined inflection during the process of decomposition indicated the occurrence of several simultaneous reactions, such as the decomposition of the ligand, its loss, and volatilization of the metal halide [23].

In the mass spectra of urea and its derivatives, the main peaks are due to the fragmentation of the nitrogen–carbon bond of the carbonyl group. Particularly, the peaks m/e 16 (NH_2), 17 (NH_3), 43 ($HNCO$), 44 (H_2NCO), and 60 (H_2NCONH_2) were observed. The analogous fragments appeared in the adducts' mass spectra. Fragmentations of mercury halides enriched their mass spectra.

The NH, CO and CN stretching frequencies of urea and adducts are listed in Table 1. The decrease in CO and an increase in CN stretching frequencies upon complexation are arguments which corroborate the coordination through oxygen of the ligand [2,8].

Based on the standard enthalpy of the general reaction (1) below, the standard enthalpies of formation of the adducts $ZnX_2 \cdot 2ur$ (X = Cl, Br, I), $CdX_2 \cdot 2ur$ (X = Br, I), $CdX_2 \cdot ur$ (X = Cl, Br, I) and $HgX_2 \cdot ur$ (X = Cl, Br) were determined. Values of $\Delta_r H_m^\ominus$ were obtained from the dissolution and reaction

$$MX_2(c) + n\,ur(c) = MX_2 \cdot n\,ur(c) \qquad \Delta_r H_m^\ominus \qquad (1)$$

and the reaction calorimetric sequence shown below using an appropriate solvent. The variation in enthalpy for each step of dissolution or reaction is

$$ur(c) + \text{calorimetric solvent} = \text{soln. A} \qquad \Delta_2 H_m^\ominus \qquad (2)$$

TABLE 2

Standard molar enthalpies of solution and reaction (kJ mol^{-1})

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m^\ominus$
2	ur (c)	EtOH [a]	A	5	13.78 ± 0.17
3	$ZnCl_2$ (c)	A	B	4	−45.04 ± 0.21
4	$ZnCl_2 \cdot 2ur$ (c)	EtOH	C	6	28.46 ± 0.14
3	$ZnBr_2$ (c)	A	B	4	−57.80 ± 0.87
4	$ZnBr_2 \cdot 2ur$ (c)	EtOH	C	5	15.39 ± 0.09
3	ZnI_2 (c)	A	B	5	−57.61 ± 0.30
4	$ZnI_2 \cdot 2ur$ (c)	EtOH	C	4	37.91 ± 0.82
2	ur (c)	MeOH [b]	A	6	12.38 ± 0.08
3	$CdCl_2$ (c)	A	B	4	−31.02 ± 0.07
4	$CdCl_2 \cdot ur$ (c)	MeOH	C	5	2.90 ± 0.15
3	$CdBr_2$ (c)	A	B	5	−24.06 ± 0.22
4	$CdBr_2 \cdot ur$ (c)	MeOH	C	4	2.20 ± 0.15
3	CdI_2 (c)	A	B	5	−25.04 ± 0.28
4	$CdI_2 \cdot ur$ (c)	MeOH	C	5	18.09 ± 0.22
3	$CdBr_2$ (c)	A	B	4	−23.64 ± 0.11
4	$CdBr_2 \cdot 2ur$ (c)	MeOH	C	5	13.14 ± 0.16
3	CdI_2 (c)	A	B	5	−25.33 ± 0.13
4	$CdI_2 \cdot 2ur$ (c)	MeOH	C	4	6.74 ± 0.08
2	$HgCl_2$ (c)	MeOH	A	6	−2.92 ± 0.08
3	ur (c)	A	B	6	11.78 ± 0.04
4	$HgCl_2 \cdot ur$ (c)	MeOH	C	6	18.25 ± 0.10
2	$HgBr_2$ (c)	EtOH–HCl [c]	A	5	31.13 ± 0.35
3	ur (c)	A	B	5	11.93 ± 0.13
4	$HgBr_2 \cdot ur$ (c)	EtOH–HCl	C	5	42.06 ± 0.69

[a] Ethanol,

[b] methanol,

[c] 1 : 1 mixture ethanol–2 M HCl.

TABLE 3

Summary of the thermochemical data for adducts (kJ mol^{-1})

Adduct	$\Delta_r H_m^\ominus$	$\Delta_f H_m^\ominus$	$\Delta_D H_m^\ominus$	$\Delta_M H_m^\ominus$	$\bar{D}$(M–O)
$ZnCl_2 \cdot 2ur$	-59.72 ± 0.30	-1142	235	384	148
$ZnBr_2 \cdot 2ur$	-59.41 ± 0.89	-1055	235	366	139
$ZnI_2 \cdot 2ur$	-81.74 ± 0.89	-957	257	377	145
$CdCl_2 \cdot ur$	-21.54 ± 0.18	-947	109	290	203
$CdBr_2 \cdot ur$	-13.88 ± 0.28	-664	102	253	165
$CdI_2 \cdot ur$	-30.75 ± 0.36	-568	118	256	168
$CdBr_2 \cdot 2ur$	-24.40 ± 0.21	-1008	200	351	132
$CdI_2 \cdot 2ur$	-19.69 ± 0.17	-890	195	333	123
$HgCl_2 \cdot ur$	-9.39 ± 0.13	-567	97	180	93
$HgBr_2 \cdot ur$	$+1.00 \pm 0.78$	-505	87	171	83

$$\text{soln. A} + MX_2(c) = \text{soln. B} \qquad \Delta_3 H_m^\ominus \tag{3}$$

$$MX_2 \cdot n\text{ur}(c) + \text{calorimetric solvent} = \text{soln. C} \qquad \Delta_4 H_m^\ominus \tag{4}$$

$$\text{soln. B} = \text{soln. C} \qquad \Delta_5 H_m^\ominus \tag{5}$$

summarized in Table 2. The $\Delta_r H_m^\ominus$ values were derived by applying the Hess law, i.e., $\Delta_r H_m^\ominus = \Delta_2 H_m^\ominus + \Delta_3 H_m^\ominus - \Delta_4 H_m^\ominus$, where $\Delta_5 H_m^\ominus = 0$. This general procedure was modified for the mercury compounds; the halides were dissolved firstly (Table 2) to attain the best variation of enthalpies.

With the exception of the complex $HgBr_2 \cdot ur$, all $\Delta_r H_m^\ominus$ values are exothermic. From these values listed in Table 3, the standard molar enthal-

TABLE 4

Auxiliary data (kJ mol^{-1})

	$\Delta_f H_m^\ominus$	Ref.	$\Delta_{sub} H_m^\ominus$	Ref.
$ZnCl_2$	-415.1	a	149.0	a
$ZnBr_2$	-328.7	a	131.0	b
ZnI_2	-208.0	a	120.0	b
$CdCl_2$	-391.5	a	181.2	c
$CdBr_2$	-316.3	a	151.5	b
CdI_2	-203.3	a	137.7	b
$HgCl_2$	-224.3	a	83.3	b
$HgBr_2$	-170.7	a	84.1	d
ur	-333.51	a	87.65	e

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pies of formation of the adducts in solid form (also listed in Table 3) were calculated using the standard enthalpies of formation of urea and of the metal halides as auxiliary data (Table 4). The standard molar enthalpies of decomposition (eqn. (6)) and the standard molar lattice enthalpies (eqn. (7)) were also calculated, by applying the auxiliary data of Table 4, in the

$$MX_2 \cdot n\mathrm{ur(c)} = MX_2(\mathrm{c}) + n\mathrm{ur(g)} \qquad \Delta_D H_m^{\ominus} \tag{6}$$

$$MX_2 \cdot n\mathrm{ur(c)} = MX_2(\mathrm{g}) + n\mathrm{ur(g)} \qquad \Delta_M H_m^{\ominus} \tag{7}$$

expressions: $\Delta_D H_m^{\ominus} = -\Delta_r H_m^{\ominus} + n\Delta_{sub} H_m^{\ominus}(\mathrm{ur})$ and $\Delta_M H_m^{\ominus} = \Delta_D H_m^{\ominus} + \Delta_{sub} H_m^{\ominus}(MX_2)$. In these expressions $\Delta_{sub} H_m^{\ominus}$ is the standard molar enthalpy of sublimation [22,23].

DISCUSSION

Due to the presence of hydrogen bonds, urea exhibits an infrared spectrum with a large splitting of the NH stretching frequency. The same splitting was shown by all adducts at higher frequencies. The strong bands at 1680 and 1450 cm^{-1} in the uncomplexed molecule were attributed to the CO stretching frequency and CN stretching vibration or amide II band, respectively [24,25]. Both bands retain their intensities in the complexes but shift on co-ordination in opposite directions [2,26]. The decrease of νCO, the increase of νCN and the splitting of the νNH to high frequencies all indicate that the urea is co-ordinating the metals by its carbonyl group [2]. This mode of co-ordination was elucidated by X-ray diffraction study of the octahedral structure of $CdCl_2 \cdot 2$ur [12].

The standard molar enthalpies of the adducts in the condensed phase ($\Delta_r H_m^{\ominus}$) were obtained by dissolution of urea, its reaction with metal halide and dissolution of the adduct. The processes of dissolution $\Delta_2 H_m^{\ominus}$ and $\Delta_4 H_m^{\ominus}$ are endothermic and the reaction leads to an exothermic value $\Delta_3 H_m^{\ominus}$. For mercury adducts this general procedure was changed; the halide was first dissolved in the calorimetric solvent, followed by the reaction process with urea and the adduct was finally dissolved in the same calorimetric solvent. In this case $\Delta_2 H_m^{\ominus}$ is exothermic for chloride and endothermic for bromide. In the reaction process, the dissolution of the urea dominates the exothermicity of the reaction, resulting in an endothermic value. All these enthalpic values are listed in Table 2. The combination of the partial enthalpic results gave $\Delta_r H_m^{\ominus}$ values, which are shown in Table 2. With the exception of the mercury bromide adduct ($\Delta_r H_m^{\ominus} = 1.00 \pm 0.78$ kJ mol^{-1}), all adducts show an exothermic value for this parameter.

The donor strength of the ligand toward specific acceptors is illustrated by means of $\Delta_r H_m^{\ominus}$ values, which reflect the Lewis acidity of metal halides of the zinc group elements [17–19,22,27], taking into account that comparisons of acid–base strengths should be made for adducts of the same stoichiometries, where crystal enthalpies, reorganization enthalpies, etc, can be assumed to be the same. Firstly, for bis-adducts this enthalpy is higher than those of cadmium complexes (Table 3), indicating a relatively higher acceptor acidity of the former metal. Within the zinc halides the acidity order is $ZnI_2 > ZnCl_2 \sim ZnBr_2$. The same behaviour is observed for iodide in the adducts of cadmium. For mono-adducts one can establish the acidity order $CdI_2 > CdCl_2 > CdBr_2 > HgCl_2 > HgBr_2$.

The shift of CO stretching frequency of urea and urea derivatives upon complexation with $SnCl_4$ or $SnBr_4$ was a property used to estimate the basicity. From these results the following order: tetramethylurea (tmu) > *N*,*N*′-dimethylurea (dmu) > *N*,*N*-dimethylurea > urea was established [28,29]. From the point of view of the thermochemical data, a comparison of the basicity of a series of bases can be made by using a sequence of adducts of the same stoichiometry: $ZnX_2 \cdot 2L$ (X = Cl, Br) or $MX_2 \cdot L$ (M = Cd, Hg and X = Cl, Br), where L = tmu, dmu and methylurea (mu). Previously, the basicity order tmu > dmu > mu was obtained from $\Delta_r H_m^\ominus$ values, for each series of adducts [18]. For example, for $ZnCl_2 \cdot 2L$ the values of $\Delta_r H_m^\ominus$ are -83.13 ± 0.96, -55.28 ± 0.33 and -36.27 ± 0.51 kJ mol^{-1}, for tmu, dmu and mu, respectively. This order reflects the donor ability of the ligand in supplying electronic density due to the inductive effect of the methyl groups linked to nitrogen atoms [18].

The plot of $\Delta_r H_m^\ominus$ values against the molecular weight of the urea derivatives showed a linear dependence, see Fig. 1, which allowed the determination of the standard molar enthalpy of *N*,*N*-dimethyl-*N*′-methylurea (trmu) by interpolation, giving −69 kJ mol^{-1} for $ZnCl_2 \cdot 2trmu$. However, the $\Delta_r H_m^\ominus$ values for zinc and cadmium urea adducts, deviate from the linear correlation. The basicity order is tmu > ur > dmu > mu for bisadducts and $CdBr_2 \cdot L$, and tmu > dmu > mu > ur for $CdCl_2 \cdot L$ and mercury adducts. It seems reasonable to admit that the hydrogen bonding affects the formation of the adduct in the solid phase, the enthalpy of formation being larger when the acid is relatively hard like zinc, than it is for the soft acid mercury. The intermediate hardness of cadmium places it in both positions [30].

The standard molar enthalpies of formation $\Delta_f H_m^\ominus$(ad, c) of bis-adducts are larger, $CdBr_2 \cdot 2ur$ (−1008 kJ mol^{-1}) and $CdBr_2 \cdot ur$ (−664 kJ mol^{-1}). For a given metal a decrease of $\Delta_f H_m^\ominus$(ad, c) for the bis-adducts from chloride, $ZnCl_2 \cdot 2ur$ (−1142 kJ mol^{-1}), to iodide, $ZnI_2 \cdot 2ur$ (−957 kJ mol^{-1}) was observed. This same behaviour was also observed for the mono-adducts, $CdCl_2 \cdot ur$ (−947 kJ mol^{-1}) and $CdI_2 \cdot ur$ (568 kJ mol^{-1}) (see Table 3).

The standard molar enthalpies of decomposition of the adducts ($\Delta_D H_m^\ominus$) is related to the enthalpy involved in the rupture of the metal–ligand bond and also to the enthalpy of rearrangement of the structure of the metal

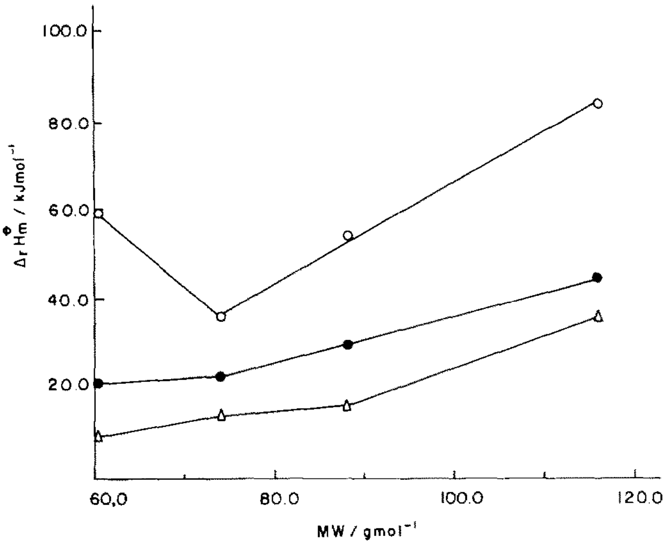

Fig. 1. $\Delta_r H_m^{\ominus}$ against molecular weight of ligand (MW): $ZnCl_2 \cdot 2L$ (○), $CdCl_2 \cdot L$ (●) and $HgCl_2 \cdot L$ (△); L = ur, mu, dmu and tmu.

halide on returning to its original form [31]. However, the standard molar enthalpies of formation of the solid adducts ($\Delta_M H_m^{\ominus}$) from reagents in gas phase contain not only the specific acid–base interactions, but also various non-specific interactions involved in the formation of these compounds [23]. Nevertheless, both parameters play important functions when combined together, because they can be used to compare and systematize adduct thermochemical data [22,23,32,33]. The variation of both parameters are very similar, $\Delta_r H_m^{\ominus}$ values being larger for bis-adducts. This trend in variation reflects the stability of these complexes, which can therefore be discussed in terms of ΔH values [34]. The bis-adducts, therefore, are more stable than the mono-adducts. For example, the adducts, $ZnBr_2 \cdot 2ur$, $CdBr_2 \cdot ur$ and $HgBr_2 \cdot ur$, present the values 235, 102, 87 and 384, 253, 171 kJ mol^{-1} for $\Delta_D H_m^{\ominus}$ and $\Delta_M H_m^{\ominus}$, respectively. The above results also show a decrease in stability from zinc to mercury.

The gas-phase data of such complexes allow metal–ligand enthalpies to be determined [22,23,33,34]. A thermochemical cycle was used to calculate the enthalpy of the reaction $MX_2(g) + n\,ur(g) = MX_2 \cdot n\,ur(g)$; $\Delta_g H_m^{\ominus}$, where $\Delta_g H_m^{\ominus}/n$ represents the mean molar enthalpy of metal–oxygen bond ($\bar{D}$), because the results are unmistakably consistent with the proposition that all adducts have the ligand bonded via its oxygen atom [2]. However, the properties of the adducts in gaseous phase are inaccessible experimentally due to the decomposition on heating (this conclusion was obtained from physical measurements such as melting points and mass spectra). In order to estimate the parameter $\bar{D}$(M–O), it was assumed that the molar enthalpy of sublimation of the adduct is equal to the molar enthalpy of sublimation of urea [17–19]. The calculated values of $\bar{D}$(M–O) are given in Table 3. The general trend of these values is similar to that of the other urea derivatives [17–19]. $\bar{D}$(M–O) for the mono-adduct $CdI_2 \cdot ur$ (168 kJ mol^{-1}) is higher than that of the corresponding bis-adduct $CdI_2 \cdot 2ur$ (123 kJ mol^{-1}). The bis-adduct of zinc, $ZnI_2 \cdot 2ur$ (145 kJ mol^{-1}) has a higher $\bar{D}$(M–O) than that of the bis-adduct of cadmium, $CdI_2 \cdot 2ur$ (123 kJ mol^{-1}). The same behaviour was observed for mono-adducts, for example, $CdBr_2 \cdot ur$ (165 kJ mol^{-1}) and $HgBr_2 \cdot ur$ (83 kJ mol^{-1}). In comparing urea and urea derivatives, $\bar{D}$(M–O) values for mercury adducts are always smaller than those of zinc and cadmium, which are similar [17–19]. This general behaviour reflects the less effective mercury–oxygen co-ordinate bond [17–19,33].

ACKNOWLEDGEMENTS

We are grateful to CAPES for a fellowship (MRMCS) and FINEP for partial financial support.

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