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Thermochemical data for adducts of ε-caprolactam with zinc(II) family metal halides

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Abstract

From solution calorimetry and appropriate thermodynamic cycles, the standard molar enthalpies of acid–base reactions in the condensed state ($\Delta_r H^\circ$) for $MX_2 \cdot nCL$ (M is Zn, Cd, Hg; X is Cl, Br, I; $n = 1, 2, 3$ or 4; CL is ε-caprolactam) adducts have been determined. From $\Delta_r H^\circ$ values and literature data, the following thermochemical quantities have been calculated: standard enthalpy of formation ($\Delta_f H^\circ$), standard enthalpy of decomposition ($\Delta_d H^\circ$), standard lattice enthalpy ($\Delta_{latt} H^\circ$), standard enthalpy of acid–base reaction in the gaseous phase ($\Delta_g H^\circ$) and the mean dissociation enthalpy of the metal–oxygen bond, $\bar{D}$(M–O). The thermochemical data are compared with those previously published for analogous BuL compounds (BuL is γ-butyrolactam or 2-pyrrolidone), with the purpose of evaluating the effect of ring strain on the donor oxygen strengths of both lactams. The thermochemical quantities are discussed in terms of acidity and basicity of the species and $\Delta_g H^\circ$ values correlated with ionic or covalent character of the metal halides.

Keywords: Metal halides; Thermochemical data; Zinc(II) family; Solution calorimetry; Adducts

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1. Introduction

Among ligands with a CO group, whose oxygen atom acts as a donor site, cyclic amides (lactams) are particularly interesting due to their structural similarity to biologically important polypeptides and proteins. Hence, the study of these species is

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useful in the attempt to elucidate the physical and chemical properties of peptidic bonds [1]. It is also interesting to mention the importance of oxygen-bonded complexes in certain biological processes, such as the replication of DNA molecules by DNA polymerase, which depends on the formation of zinc–oxygen bonds [2].

This study, which deals with the halides of the zinc family and their ε-caprolactam (CL) adducts, is a continuation of our interest in investigating the ability of lactams to form stable complexes with transition metals [3]. The $ZnX_2 \cdot nCL$ (X is Cl, Br, I; $n = 2, 3$), $CdX_2 \cdot CL$ (X is Cl, Br), $CdX_2 \cdot 2CL$ (X is Br, I), $HgX_2 \cdot CL$ (X is Cl, Br), $HgBr_2 \cdot 2CL$ and $HgI_2 \cdot 4CL$ adducts have been isolated and characterized, with the main objective focused on their thermochemical data including mean metal–oxygen bond enthalpies. Some previous studies on coordination compounds with CL have dealt with structural aspects and are mainly concerned with the coordination site [4–12]. However, there are no thermochemical studies concerning the energetics of formation of compounds with this ligand.

Generally, the thermochemical data for $MX_2 \cdot nCL$ adducts and their analogous γ-butyrolactam (BuL) adducts [3] show the relative base strength CL > BuL. This order is thought to be associated with the effect of ring strain, which is evaluated on the basis of the bond angles of these lactams. The thermochemical data in the gaseous phase are shown to be correlated with some energetic parameters of the corresponding metal halides.

2. Experimental

2.1. Chemicals

Reagent grade ε-caprolactam from Nitrocarbono S.A. was purified by distilling under reduced pressure at 393 K. $ZnCl_2$ was prepared following a literature procedure [13], $CdBr_2 \cdot 4H_2O$ was made anhydrous by heating in vacuum at 423 K for ten hours [14] and $CdCl_2 \cdot 2.5H_2O$ was dehydrated by the Christov procedure [15]. The remaining metal halides (Aldrich) were dried under vacuum before use and had approximately 98% purities, checked by analysing the metal by EDTA titration [16, 17]. All samples were manipulated in a dry nitrogen atmosphere using a glove-bag. Reagent grade solvents (Merck) were purified [18] and then stored over molecular sieves.

2.2. Preparation of the adducts

$ZnX_2 \cdot 3CL$ (X is Br, I) and $ZnX_2 \cdot 2CL$ (X is Cl, Br, I) adducts were obtained by adding the appropriate anhydrous halide (5.92, 9.14, 8.24, 9.42 and 5.86 mmol respectively), dissolved in anhydrous ethanol, to a solution of the ligand (23.7, 36.58, 18.50, 23.27 and 11.7 mmol respectively) dissolved in the same solvent. The resulting solutions were stirred and refluxed by heating at 353 K: $ZnBr_2 \cdot 3CL$ (1 h), $ZnI_2 \cdot CL$ (10 h); or at 333 K: $ZnI_2 \cdot 3CL$ (4 h), $ZnCl_2 \cdot 2CL$ (30 min) and $ZnBr_2 \cdot 2CL$ (2 h). Attempts to prepare the $ZnCl_2 \cdot 3CL$ adduct in solution, by varying reagent amounts and solvents, always gave a non-stoichiometric product. Thus, stoichiometric amounts of salt and ligand were heated at 343 K in a sealed tube immersed in a glycerine bath to obtain the $ZnCl_2 \cdot 3CL$ adduct. $CdCl_2 \cdot CL$, $CdBr_2 \cdot 2CL$ and $CdI_2 \cdot 2CL$ adducts were crystallized from an ethanolic solution of the ligand (13.87, 23.1 and 25.25 mmol respectively) to which appropriate salts were added in the respective amounts (3.49, 5.80 and 6.28 mmol), then refluxed at 333 K. To obtain the $CdBr_2 \cdot CL$ adduct, 5.98 mmol of cadmium bromide were dissolved in 20 ml of hot ethanol with stirring, then 6.30 mmol of the ligand dissolved in ethanol were added and the resulting solution was maintained under reflux for two hours. The preparation of $HgCl_2 \cdot CL$, $HgBr_2 \cdot CL$ and $HgBr_2 \cdot 2CL$ adducts consisted of slowly adding the ligand, dissolved in 20 ml of ethanol (for $HgBr_2 \cdot CL$ acetone was used) to the appropriate metal halide solution at the respective molar ratios: 1:2.5, 1:1.1 and 1:3.5. After stirring for two hours at 333 K and evaporating the solvent under vacuum, a white precipitate immediately appeared. $HgI_2 \cdot 4CL$ was obtained by adding 4.88 mmol of HgI_2 to an ethanolic solution of 39 mmol of ε-caprolactam. After two hours of stirring, the solvent was evaporated and a mixture of ethyl acetate and *n*-hexane (1:3) was added. This procedure (addition of a solvent mixture and evaporation) was repeated three times. All the adducts were filtered, washed with either *n*-hexane or ethyl acetate, or a mixture of both, and then dried under vacuum for at least 5 h ($HgI_2 \cdot 4CL$ was dried for 48 h).

2.3. *Characterization of the adducts*

The carbon, nitrogen and hydrogen contents were determined by using a Perkin-Elmer 240 Element Analyzer and the metal contents by standard methods [16, 17]. All results agreed, within the experimental error, with the proposed formulation for the adducts. Infrared spectra were obtained in the 4000–400 cm^{-1} range with a Perkin-Elmer 283 B recording spectrophotometer, using Nujol mulls. Melting points were determined in sealed capillary tubes on a HWS SG2000 apparatus and thermogravimetry determinations were carried out using a Perkin-Elmer TGA 7 thermobalance with a flux of dry nitrogen and a heating rate of 5°C min^{-1}.

2.4. *Calorimetric procedures*

Calorimetric measurements were performed using a Parr 1451 Solution Calorimeter System, at 298.15 K, in appropriate solvents. The calorimeter's performance and details of operation were described previously [3]. Ethanol, methanol and a mixture ethanol–diethanolamine were used as calorimetric solvents because of their capacities to dissolve ligand, halides and adducts.

3. Results and discussion

With the exception of $CdCl_2 \cdot CL$ and $HgI_4 \cdot 4CL$, all adducts are soluble in ethanol and very sensitive to moisture; thus all manipulations were carried out in a dry nitrogen atmosphere. The melting points and main infrared bands are summarized in Table 1. For $ZnCl_2 \cdot 3CL$, $ZnCl_2 \cdot 2CL$, $ZnBr_2 \cdot 3CL$, $ZnBr_2 \cdot 2CL$, $ZnI_2 \cdot 2CL$, $HgCl_2 \cdot CL$ and

Table 1
Melting points and absorption frequencies (cm^{-1}) of the CONH group of $MX_2 \cdot n CL$ adducts

Compounds	ν(NH)	Δν(NH)	ν(CO)	Δν(CO)	m.p./K
CL	3219		1660		
$ZnCl_2 \cdot 2CL$	3288	+69	1627	−33	382.7–384.0
$ZnCl_2 \cdot 3CL$	3286	+67	1635	−25	342.1–343.9
$ZnBr_2 \cdot 2CL$	3244	+25	1630	−30	378.8–379.1
$ZnBr_2 \cdot 3CL$	3250	+31	1639	−21	354.0–355.0
$ZnI_2 \cdot 2Cl$	3286	+67	1627	−33	382.8–383.0
$ZnI_2 \cdot 3CL$	3236	+17	1630	−30	404.1–404.8
$CdCl_2 \cdot CL$	3287	+68	1630	−30	*
$CdBr_2 \cdot CL$	3291	+72	1622	−38	*
$CdBr_2 \cdot 2CL$	3245	+26	1622	−38	401.5–402.3
$CdI_2 \cdot 2CL$	3238	+19	1622	−38	404.1–404.8
$HgCl_2 \cdot CL$	3287	+68	1620	−40	404.7–405.0
$HgBr_2 \cdot CL$	3273	+64	1630	−30	388.6–388.9
$HgBr_2 \cdot 2CL$	3274	+55	1635	−25	370.3–371.1
$HgI_2 \cdot 4CL$	3261	+42	1640	−20	343.0–344.2

* Did not melt until 523 K.

$HgBr_2 \cdot CL$ adducts reproducible melting points were observed after cooling the melted samples and subsequently reheating. Thermogravimetric determinations confirmed that the beginning of the decomposition of these compounds occurred at temperatures higher than the melting point range. The $CdCl_2 \cdot CL$ and $CdBr_2 \cdot CL$ adducts did not melt until 523 K, although thermogravimetric results showed that the first step of mass loss occurs at approximately 440 K. For $CdBr_2 \cdot 2CL$, $CdI_2 \cdot 2CL$, $HgBr_2 \cdot 2CL$ and $HgI_2 \cdot 4CL$ adducts, the melting points are not reproducible because of the decomposition during heating. From the thermogravimetric curves, it was observed that the mass loss was consistent with the stoichiometry of these compounds, except for the mercury adducts which lost mass continuously, without any perceivable inflection.

The wavenumber of the CO stretch for all adducts decreases in relation to that of the free ligand, indicating that coordination occurs through the oxygen atom. The ν(NH) in the infrared spectra of the adducts is higher than that observed in the spectrum of the uncomplexed ε-caprolactam, due to the formation of hydrogen bonds between the NH group of the CL and the halide anion.

The standard enthalpy of the reaction: $MX_2(s) + nCL(s) = MX_2 \cdot nCL(s)$, $\Delta_r H^\circ$, was obtained through the following standard enthalpies of the reactions in solution

$MX_2(s)$ + calorimetric solvent = MX_2(solvent) $\Delta_1 H^\circ$
$nCL(s) + MX_2(\text{solvent}) = MX_2 \cdot nCL(\text{solvent})$ $\Delta_2 H^\circ$
CL(s) + calorimetric solvent = CL(solvent) $\Delta_3 H^\circ$
$MX_2(s) + nCL(\text{solvent}) = MX_2 \cdot nCL(\text{solvent})$ $\Delta_4 H^\circ$
$MX_2 \cdot nCL(s)$ + calorimetric solvent = $MX_2 \cdot nCL$(solvent) $\Delta_5 H^\circ$

The previously obtained $\Delta_1 H^\circ$ values [19,20] and the other dissolution enthalpies, $\Delta_2 H^\circ$–$\Delta_5 H^\circ$, are listed in Table 2. The values were obtained by applying the least

Table 2
Dissolution enthalpy values (kJ mol^{-1})

Adducts	Δ_1H°	Δ_2H°	Δ_3H°	Δ_4H°	Δ_5H°	
$ZnCl_2 \cdot 2CL$	$-43.10 \pm 0.27^{a,b}$	$+15.33 \pm 0.80$			$+47.85 \pm 0.74$	Ethanol
$ZnCl_2 \cdot 3CL$	$-43.10 \pm 0.27^{a,b}$	$+7.77 \pm 0.05$			$+50.32 \pm 0.13$	Ethanol
$ZnBr_2 \cdot 2CL$			$+14.13 \pm 0.26$	-33.86 ± 0.26	$+36.76 \pm 0.39$	Ethanol
$ZnBr_2 \cdot 3CL$			$+14.13 \pm 0.26$	-43.24 ± 0.08	$+69.44 \pm 0.10$	Ethanol
$ZnI_2 \cdot 2CL$			$+14.13 \pm 0.26$	-35.47 ± 0.09	$+31.51 \pm 0.09$	Ethanol
$ZnI_2 \cdot 3CL$			$+14.13 \pm 0.26$	-42.31 ± 0.18	$+67.76 \pm 0.82$	Ethanol
$CdCl_2 \cdot CL$	$-18.30 \pm 0.15^{a,b}$	$+9.01 \pm 0.14$			$+18.40 \pm 0.87$	Methanol
$CdBr_2 \cdot CL$	$-6.13 \pm 0.12^{1,b}$	$+8.76 \pm 0.07$			$+16.43 \pm 0.06$	Ethanol
$CdBr_2 \cdot 2CL$	$-6.13 \pm 0.12^{a,b}$	$+5.63 \pm 0.09$			$+37.89 \pm 0.23$	Ethanol
$CdI_2 \cdot 2CL$			$+14.13 \pm 0.26$	-21.06 ± 0.23	$+32.22 \pm 0.09$	Ethanol
$HgCl_2 \cdot CL$			$+14.13 \pm 0.26$	$+4.79 \pm 0.29$	$+32.82 \pm 0.60$	Ethanol
$HgBr_2 \cdot CL$	$+3.14 \pm 0.03^{a,b}$	$+8.71 \pm 0.59$			$+30.25 \pm 0.32$	Ethanol
$HgBr_2 \cdot 2CL$	$+3.14 \pm 0.03^{a,b}$	$+10.76 \pm 0.13$			$+46.27 \pm 0.14$	Ethanol
$HgI_2 \cdot 4CL$	-22.59 ± 0.09^{c}	-5.55 ± 0.05			$+51.31 \pm 0.14$	*

[a,b] Refs. [19, 20] [c] From our laboratory. * Ethanol + 20% diethanolamine.

square method [21] to at least six individual determinations. From these values, Δ_rH° can be obtained by applying Hess's law: $\Delta_rH^\circ = \Delta_1H^\circ + \Delta_2H^\circ - \Delta_5H^\circ$; $\Delta_rH^\circ = n\Delta_3H^\circ + \Delta_4H^\circ - \Delta_5H^\circ$. The choice of the appropriate thermodynamic cycle to calculate Δ_rH° was determined according to the best experimental conditions, such as the solubility of reagents and the thermal effect values produced.

Using Δ_rH° values and the auxiliary data listed in Table 3 [22–26], the values of $\Delta_fH^\circ(MX_2 \cdot nCL) = \Delta_rH^\circ + n\Delta_fH^\circ(CL) + \Delta_fH^\circ(MX_2)$ were calculated. The standard molar enthalpies of decomposition (Eq. (1)), $\Delta_dH^\circ(MX_2 \cdot nCL) = -\Delta_rH^\circ + n\Delta_{sub}H^\circ$ (CL), and the standard molar lattice enthalpies (Eq. (2)), $\Delta_{latt}H^\circ(MX_2 \cdot nCL) = \Delta_dH^\circ + \Delta_{sub}H^\circ(MX_2)$, were also calculated by applying the auxiliary data of Table 3. In these expressions $\Delta_{sub}H^\circ$ is the standard molar enthalpy of sublimation

$$MX_2 \cdot nCL(s) = MX_2(s) + nCL(g) \quad \Delta_dH^\circ \tag{1}$$

$$MX_2 \cdot nCL(s) = MX_2(g) + nCL(g) \quad \Delta_{latt}H^\circ \tag{2}$$

To obtain Δ_gH°, and consequently $\bar{D}$(M–O), the following thermochemical cycle was applied

$$\begin{tikzcd}
MX_2(g) & + & nCL(g) \arrow[r, "\Delta_gH^\circ"] & MX_2nCL(g) \\
MX_2(s) \arrow[u, "\Delta_{sub}H^\circ(MX_2)"'] & + & nCL'(s) \arrow[u, "n\Delta_{sub}H^\circ(CL)"'] \arrow[r, "\Delta_rH^\circ"] & MX_2nCL(s) \arrow[u, "\Delta_{sub}H^\circ(MX_2nCL)"']
\end{tikzcd}$$

from which one derives
$\Delta_gH^\circ(MX_2 \cdot nCL) = \Delta_rH^\circ + \Delta_{sub}H^\circ(MX_2 \cdot nCL) - n\Delta_{sub}H^\circ(CL) - \Delta_{sub}H^\circ(MX_2)$
Values for $\Delta_{sub}H^\circ$(CL) and $\Delta_{sub}H^\circ(MX_2)$ are available in the literature (see Table 3), so

Table 3
Auxiliary thermochemical data

Compounds	$-\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_{sub}H^\circ$/kJ mol^{-1}
CL(s)	329.4[a]	83.3[b]
$ZnCl_2$	415.1[b,c]	149.0[b]
$CdCl_2$	391.5[b,c]	181.2[d]
$HgCl_2$	224.3[b,c]	83.3[e]
$ZnBr_2$	328.7[b,c]	131.0[e]
$CdBr_2$	316.2[b,c]	151.5[d]
$HgBr_2$	170.7[b,c]	84.1[e]
ZnI_2	208.0[b,c]	120.0[d]
CdI_2	203.3[b,c]	137.7[d]
HgI_2	105.4[d]	88.2[e]

[a] Ref. [22]. [b] Ref. [23]. [c] Ref. [24]. [d] Ref. [26]. [e] Ref. [25].

that it is necessary only to obtain the enthalpy of sublimation of the adducts. Since these adducts dissociate when heated to temperatures at which it is possible to measure their vapour pressures, $\Delta_g H^\circ(MX_2 \cdot nCL)$ is not experimentally accessible.

Thus, in order to obtain $\Delta_g H^\circ(MX_2 \cdot nCL)$, the approximation which establishes the enthalpy of sublimation of the adduct as equal to the enthalpy of sublimation or vaporization of the ligand was utilized [27]. Burkinshaw and Mortimer [2, 28] present arguments in favour of this assumption based on the available enthalpies of sublimation of some thiourea adducts of the type $MCl_2 \cdot 4tu$ [29] and other sublimable adducts, whose enthalpy values are close to that of the ligand, varying within ± 10 kJ mol^{-1}, i.e. within the experimental error. Statistical correlation to support this assumption has been made [30] and more arguments are given by using other extra-thermodynamic means [31]. Based on this assumption, the mean metal bond enthalpies for nearly one hundred compounds have been determined [27].

The values of the mean enthalpy of dissociation of the metal–oxygen bond, $\bar{D}(M\text{–}O)$, were determined from its relation with $\Delta_g H^\circ$, according to

$$\bar{D}(M\text{–}O) = -\Delta_g H^\circ / n \qquad (3)$$

The thermochemical data for all $MX_2 \cdot nCL$ adducts are summarized in Table 4. In considering $\Delta_r H^\circ$ values, which reflect the Lewis acidities of a group of metal halides [32], comparisons should be made for adducts of the same stoichiometry in which crystal enthalpies, reorganization enthalpies, etc., can be assumed to be the same. With the zinc halides, the acidity order $ZnCl_2 > ZnBr_2 > ZnI_2$ is observed. Comparing the adducts of the same stoichiometry, the relative acidity order decreases from zinc to mercury.

The values of $\Delta_d H^\circ(MX_2 \cdot nCL)$ show that the intensity of metal–ligand interaction decreases in the order Zn > Cd > Hg, for the majority of the adducts. Concerning $\Delta_{latt}H^\circ$ and $\Delta_g H^\circ$, their values also establish that the donor–acceptor interaction decreases from zinc to mercury, except for $ZnBr_2 \cdot 2CL$, $CdBr_2 \cdot 2CL$, $ZnI_2 \cdot 2CL$ and $CdI_2 \cdot 2CL$, where a Cd > Zn order is verified. $\bar{D}(M\text{–}O)$ values show that the energetic

Table 4
Summary of the thermochemical results for $MX_2 \cdot nL$ (L is CL and BuL) adducts

Adducts	$-\Delta_r H^\circ$		$-\Delta_f H^\circ$		$\Delta_d H^\circ$		$-\Delta_{latt} H^\circ$		$-\Delta_g H^\circ$		$\bar{D}$(M—O)	
	L is CL	L is BuL	L is CL	L is BuL	L is CL	L is BuL	L is CL	L is BuL	L is CL	L is BuL	L is CL	L is BuL
$ZnCl_2 \cdot 3L$	85.79 ± 0.30	105.05 ± 0.33	1489	1379	336	230	485	379	401	337	134	112
$ZnCl_2 \cdot 2L$	75.66 ± 1.12	73.33 ± 0.38	1149	1061	242	157	391	306	308	264	154	132
$CdCl_2 \cdot L$	27.65 ± 1.57	30.72 ± 0.24	749	708	111	72	292	254	208	212	208	212
$HgCl_2 \cdot L$	13.90 ± 0.72	28.21 ± 0.23	568	539	97	70	180	153	97	111	97	111
$ZnBr_2 \cdot 3L$	70.29 ± 0.30	101.02 ± 0.52	1387	1188	320	226	451	357	368	315	123	105
$ZnBr_2 \cdot 2L$	42.31 ± 0.54	71.33 ± 0.50	1129	972	209	155	339	286	257	244	128	122
$CdBr_2 \cdot 2L$	38.39 ± 0.27		1013		205		356		273		136	
$CdBr_2 \cdot L$	13.80 ± 0.15	39.30 ± 0.25	659	642	97	81	249	232	165	191	165	191
$HgBr_2 \cdot 2L$	32.37 ± 0.19		862		199		283		200		100	
$HgBr_2 \cdot L$	18.34 ± 0.67	24.81 ± 0.31	518	482	102	66	186	151	102	109	102	109
$ZnI_2 \cdot 3L$	67.69 ± 1.03	106.06 ± 0.39	1264	1173	318	231	438	351	354	309	118	103
$ZnI_2 \cdot 2L$	38.72 ± 0.29	75.40 ± 0.35	905	856	205	159	325	279	242	237	121	118
$CdI_2 \cdot 2L$	25.03 ± 0.36	50.03 ± 0.25	887	826	192	133	329	271	246	229	123	114
$HgI_2 \cdot 4L$	79.45 ± 0.17		1052		412		501		417		104	

interactions in the adducts follow the sequence: Zn < Cd < Hg, and decrease throughout halide series in the order: Cl > Br > I, except for $HgCl_2 \cdot CL$ and $HgBr_2 \cdot CL$, where Cl < Br is observed.

Throughout the thermodynamic results (see Table 4), we can verify that the thermochemical behavior of the adducts dealt with in this work shows agreement with that observed for analogous BuL adducts [3], confirming, in a general way, the Zn > Cd > Hg acidity sequence.

Concerning the basicity of CL and BuL, a comparison of $\Delta_r H^\circ$ values for analogous adducts of these lactams shows a BuL > CL basicity order, in contrast to the inverse order, CL > BuL, verified from $\Delta_f H^\circ$, $\Delta_d H^\circ$ and $\Delta_{latt} H^\circ$ values. The basicity order CL > BuL is consistent with that observed by Bright et al. [5], who evaluated the effect of ring size on the donor strengths of γ-butyrolactam (ring of 5 members), δ-valerolactam (ring of 6 members) and ε-caprolactam (ring of 7 members), based on the ligand field parameter, D_q. The D_q values for Ni(II) complexes of the mentioned lactams suggested the following basicity sequence: 5 < 6 ≅ 7-membered ring.

The donor capacity of lactams is thought to be associated with the effect of ring strain. The basicity order CL > BuL is also supported by the study of Bartlett and Stiles [33], which explains, in terms of the hybridization of the carbon atom in a carbonyl group, the oxygen donor ability of various cyclic compounds that contain a CO group. When the ring is contracted, the ring bonds to the carbon atom in the carbonyl group become more p in character, which confers more s (tripe bond) character to the C=O bond [34]. Since the s-bonds are more electronegative than the p-bonds [35], the oxygen becomes a poorer electron donor. The bond angles [36] in Figs. 1 and 2 confirm the approximately sp^2 (127.1°C) and sp^3 (108.4°C) configurations for the carbonyls of CL and BuL, respectively.

From the arguments presented, perhaps it would be more consistent to consider that the $\Delta_f H^\circ$, $\Delta_d H^\circ$ and $\Delta_{latt} H^\circ$ quantities are more appropriate than $\Delta_r H^\circ$ to give the information sought here. However, it is important to emphasize that the $\Delta_r H^\circ$, $\Delta_f H^\circ$ and $\Delta_d H^\circ$ quantities include the effects of the solid state. $\Delta_{latt} H^\circ$ is more associated with the reaction in the gaseous phase and, therefore, its values must reflect a greater contribution from donor–acceptor interactions.

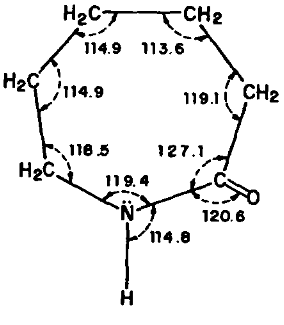

Fig. 1. ε-Caprolactam.

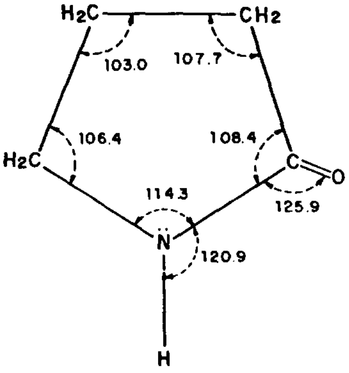

Fig. 2. γ-Butyrolactam.

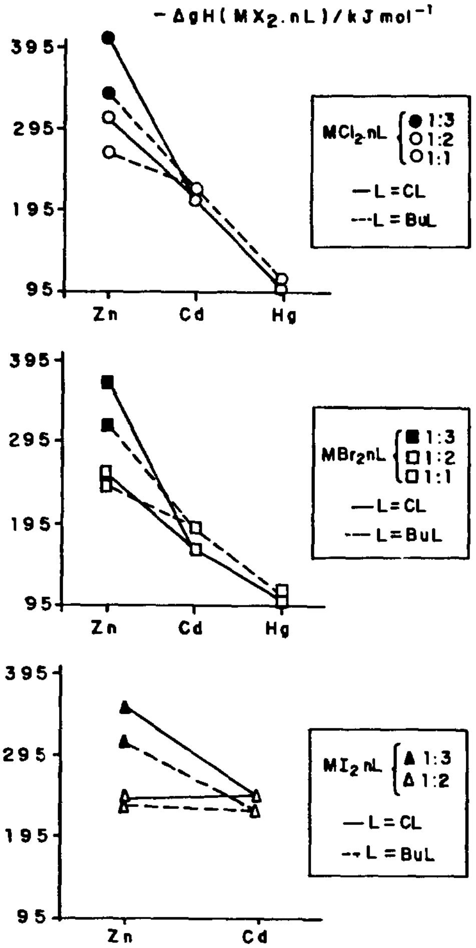

Fig. 3. Variation of $\Delta_g H^\circ$ values in the zinc(II) family for $MX_2 \cdot nL$ (L is CL and BuL) adducts.

$\Delta_g H^\circ$ and $\bar{D}$(M–O) should be the best thermodynamic quantities to characterize the donor–acceptor interaction since, in the ideal gaseous state, the contributions due to intermolecular forces are removed. From their values, the basicity order $ZnX_2 \cdot n$CL > $ZnX_2 \cdot n$BuL is observed. However, when the acid of reference is cadmium or mercury, a greater facility for coordination with BuL is observed, although the exception for the $CdI_2$2CL and $CdI_2 \cdot$2BuL adducts must be verified. The variations of $\Delta_g H^\circ$ and $\bar{D}$(M–O) values in the zinc(II) family for $MX_2 \cdot n$L (L is CL and BuL) adducts can be better observed in Figs. 3 and 4.

The possible influence of the ionic and covalent character of the metal halides in these donor–acceptor interaction processes has been investigated. There is some correlation of the bond energy of the metal halides with $\Delta_g H^\circ$ values, but this requires further study. It is probable that the preference of a determined metal halide for a determined lactam is related to its percent ionic character, $\%E_i(MX_2)$, or percent

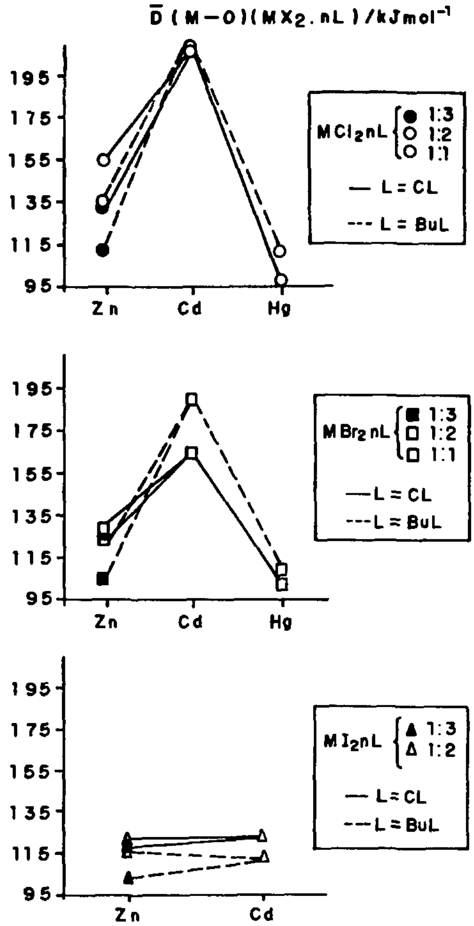

Fig. 4. Variation of $\bar{D}$(M–O) values in the zinc(II) family for $MX_2 \cdot n$L (L is CL and BuL) adducts.

Table 5
Bond energy in metal halides and $\Delta_g H^\circ(MX_2 \cdot nL)$ values

Halides	bond energy/kJ mol^{-1}		Adducts	$-\Delta_g H^\circ$	
	$\%E_i^a$	$\%E_c^a$		L is CL	L is BuL
ZnI_2	31.8	68.2	$ZnI_2 \cdot 3L$	354	309
			$ZnI_2 \cdot 2L$	242	237
CdI_2	42.1	57.9	$CdI_2 \cdot 2L$	246	229
$ZnBr_2$	45.9	54.1	$ZnBr_2 \cdot 3L$	368	315
			$ZnBr_2 \cdot 2L$	257	244
$ZnCl_2$	51.2	48.8	$ZnCl_2 \cdot 3L$	401	337
			$ZnCl_2 \cdot 2L$	308	264
$CdBr_2$	53.8	46.2	$CdBr_2 \cdot L$	165	191
$CdCl_2$	58.3	41.7	$CdCl_2 \cdot L$	208	212
$HgBr_2$	62.0	38.0	$HgBr_2 \cdot L$	102	109
$HgCl_2$	66.8	33.2	$HgCl_2 \cdot L$	97	111

[a] Ref. [37].

covalent character, $\%E_c(MX_2)$, of the bond energy of the metal halides. On examining $\%E_i(MX_2)$ and $\%E_c(MX_2)$ values [37] and comparing them with $\Delta_g H^\circ$ values for the corresponding CL and BuL compounds (see Table 5), it is verified that the metal halides that have a greater coordination capacity with CL possess a greater $\%E_c$, while BuL prefers those with a greater ionic character. We hope that this correlation study may prompt further interest in this aspect of coordination studies.

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