Thermochemistry of Dichlorobis(*NN*-dimethylacetamide)-zinc(II), and Dichloro(*NN*-dimethylacetamide)-cadmium(II) and -mercury(II)

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The standard enthalpy change ($\Delta H_R^\ominus$) for the reaction $MCl_2(s) + nDMA(l) \longrightarrow [MCl_2(DMA)_n]$ (s) (M = Zn, $n = 2$; M = Cd or Hg, $n = 1$; DMA = *NN*-dimethylacetamide) as measured by solution calorimetry gave values −84.2 ± 1.6 (Zn), −29.2 ± 0.2 (Cd), and 25.2 ± 0.7 (Hg) kJ mol^{-1}, respectively. The values of the standard enthalpy of formation ($\Delta H_f^\ominus$) of the adducts were determined from values of $\Delta H_R^\ominus$, and the standard enthalpies of formation of *NN*-dimethylacetamide and the metal chlorides, giving the values −1 055 ± 5, −698 ± 2, and −527 ±2 kJ mol^{-1} for zinc, cadmium, and mercury, respectively.

MUCH attention has been devoted to the study of amides, not only from the point of view of co-ordination but also in relation to their structural behaviour, since amides can be visualized as a good model for the peptide bond.[1] *NN*-Dimethylacetamide (DMA) is a versatile ligand which has interesting co-ordination properties, as well as being a non-aqueous solvent.[2,3] It is a highly polar solvent which does not ionize to any significant extent, and its high donor number[4] enables it to co-ordinate strongly with cations,[5-13] without forming a hydrogen bond with anions.[14]

DMA has either the oxygen or the hindered nitrogen which can bond to metals. The characteristics presented by hard acceptors[15] result in co-ordination to oxygen. However, soft acids such as gold in $H[AuX_4(DMA)_2]$ co-ordinate to nitrogen, and the hard proton bridges both oxygens.[16] Considering zinc, cadmium, and mercury, which are the main concern, of this study, the hardness changes along the group, but not abruptly, so that all are co-ordinated through oxygen. An *X*-ray diffraction study of dichlorobis(*NN*-dimethylacetamide)zinc(II) shows that the metal is bonded to oxygen in a tetrahedral environment.[12]

In the literature of donor–acceptor complexes, especially of the hydrogen-bonded variety, DMA is often employed. Thermodynamic data of equilibrium of a series of acid–base interactions have been obtained by various procedures.[17-22]

In spite of the large amount of work on the structures of adducts of amides, to our knowledge only the thermochemistry of adducts of *N*-(2-pyridyl)acetamide[23] with the zinc triad has been studied. The thermochemistry of the metal–sulphur bond has been estimated in adducts of thiourea, using solution calorimetry.[24]

The thermochemical data[25] for the adducts of triphenylphosphine oxide, wherein the enthalpy of sublimation of the adducts is related to the enthalpy of the solid ligand, enabled us to tackle the problem of estimating the enthalpy of the metal–oxygen bond. Determination of the enthalpy of sublimation of the adduct is not possible because the compound only exists in the solid state.

In this paper, the thermochemistry of the compounds $[ZnCl_2(DMA)_2]$, $[CdCl_2(DMA)]$, and $[HgCl_2(DMA)]$ has been determined through solution calorimetry.

EXPERIMENTAL

Materials and Preparations.—Analytical grade materials were used throughout. The intermediate fraction of *NN*-dimethylacetamide (Merck) was collected, after purification and distillation through an efficient column.[22] The anhydrous zinc and cadmium chlorides were prepared as described previously.[26,27] Anhydrous mercury chloride (E. Merck) was used without further purification. The adducts were prepared according to the literature;[5] their purity was confirmed by i.r. spectroscopy, and satisfactory metal and chloride analyses.

Calorimetric Measurements.—The LKB 8700 precision calorimetric system supplied with a strip-chart recorder (Servoger S) was used, following the previous procedure.[25] The salts and adducts were rigorously dried *in vacuo* before preparing the ampoules, which were handled in a dry box for the *air-sensitive* compounds. Ampoules containing 10—100 mg of substrate were broken into the glass vessel, which was charged with 90.0 ml of calorimetric solvent (which had the capacity to dissolve completely ligand, salts, and adducts). All measurements were performed at 298.15 ± 0.02 K, and at least five runs were employed for each calorimetric determination.

Other Measurements.—Melting points were obtained in sealed capillaries. Thermogravimetric determinations were made using a Perkin-Elmer TGS-1 thermobalance with a heating rate of 5 °C min^{-1} and purged with dry nitrogen. The i.r. spectra were recorded as Nujol and Fluorolube mulls on a Perkin-Elmer 337 spectrophotometer. The mass spectra of ligand and adducts were recorded on a Finnigan 1015 S/L instrument, and the ^1H n.m.r. spectra were obtained on a Varian T-60 spectrometer.

RESULTS

The melting point and thermogravimetric determinations showed the decomposition of the adducts during melting. The zinc adduct started to lose mass at 113 °C, which is near its melting point of 119—120 °C, and continued to complete the loss of two ligands and metal chloride at 420 °C. The cadmium adduct melted at 80—82 °C and the thermogram presented a loss of mass between 81—202 °C, which corresponded to the loss of the ligand (weight loss-found 32.2%; calculated 32.4%); the cadmium chloride completed its vaporization at 515 °C. The mercury adduct, which melted at 93—95 °C, released the ligand in the range 60—117 °C, and completed vaporization at 189 °C.

The mass spectra of the adducts were obtained around 20 °C above and below the melting point, and no parent ion was detected. The mass spectrum of DMA at 40 °C showed the following peaks (fragments in parentheses): *m/e* 87 ($MeCONMe_2$), 72 (MeCONMe), 57 (MeCON), 44 (MeNMe), and 43 (MeCO), the same fragments being observed for all adducts. In the case of the mercury adduct the fragmentation of mercury chloride, *m/e* 268/274 ($HgCl_2$), 233/237 (HgCl), and 199/202 (Hg) was also observed.

The ^1H n.m.r. spectrum of a stoicheiometric mixture of $HgCl_2$ and DMA, and [$HgCl_2$(DMA)] in 1,2-dichloroethane, did not show any change in position of the hydrogen resonance compared with free DMA [28,29] in the same solvent.

The values of the standard enthalpy $\Delta H_R^\ominus$ of reaction (1)

$$MCl_2(s) + nDMA(l) \xrightarrow{\Delta H_R^\ominus} [MCl_2(DMA)_n](s) \quad (n = 1 \text{ or } 2) \qquad (1)$$

were obtained through the standard enthalpies of reactions (2)—(7).

$$MCl_2(s) + \text{Calorimetric solvent} \xrightarrow{\Delta H_2^\ominus} \text{solution A} \qquad (2)$$

$$nDMA(l) + \text{solution A} \xrightarrow{\Delta H_3^\ominus} \text{solution B} \qquad (3)$$

$$nDMA(l) + \text{Calorimetric solvent} \xrightarrow{\Delta H_4^\ominus} \text{solution A}' \qquad (4)$$

$$MCl_2(s) + \text{solution A}' \xrightarrow{\Delta H_5^\ominus} \text{solution B} \qquad (5)$$

$$[MCl_2(DMA)_n](s) + \text{Calorimetric solvent} \xrightarrow{\Delta H_6^\ominus} \text{solution C} \qquad (6)$$

$$\text{Solution B} \xrightarrow{\Delta H_7^\ominus = 0} \text{solution C} \qquad (7)$$

$\Delta H_R^\ominus$ Values can be derived conveniently by applying Hess' law to the above reactions. Thus, $\Delta H_R^\ominus = \Delta H_2^\ominus + \Delta H_3^\ominus - \Delta H_6^\ominus$ or $\Delta H_R^\ominus = \Delta H_4^\ominus + \Delta H_5^\ominus - \Delta H_6^\ominus$. Both procedures could be used to derive $\Delta H_R^\ominus$; however, the choice was made on the basis of the ease in obtaining the best final result. The enthalpies of dissolution of the metal chlorides, DMA, and the adducts are listed in Table 1. Values of $\Delta H_R^\ominus$ and the standard enthalpies of formation of adducts ($\Delta H_f^\ominus$) are summarized in Table 2. The value of $\Delta H_f^\ominus$ was determined from the enthalpy of formation of metal chlorides [30] MCl_2 (M = Zn, Cd, or Hg), the enthalpy of formation of ligand [31] (−278.1 ± 1.5 kJ mol^{-1}), and $\Delta H_R^\ominus$ obtained for reaction (1).

TABLE 1

Enthalpies of dissolution at 298 K

Substance	Calorimetric solvent	$\Delta H^\ominus$/kJ mol^{-1}
$ZnCl_2$	Solution of DMA in dioxan	−46.63 ± 1.03
$CdCl_2$	Methanol	−18.30 ± 0.15
$HgCl_2$	1,2-Dichloroethane	13.40 ± 0.30
$HgCl_2$	Solution of DMA in ethanol	4.24 ± 0.05
DMA	Dioxan	2.39 ± 0.03
DMA	Ethanol	−3.25 ± 0.08
DMA	Solution of $CdCl_2$ in methanol	−5.00 ± 0.05
DMA	Solution of $HgCl_2$ in dichloroethane	−2.97 ± 0.04
[$ZnCl_2(DMA)_2$]	Dioxan	42.36 ± 0.46
[$CdCl_2$(DMA)]	Methanol	5.90 ± 0.03
[$HgCl_2$(DMA)]	1,2-Dichloroethane	35.38 ± 0.32
[$HgCl_2$(DMA)]	Ethanol	25.92 ± 0.20

TABLE 2

Thermochemical results

Compound	$\Delta H_f^\ominus$/kJ mol^{-1}	$\Delta H_R^\ominus$/kJ mol^{-1}
[$ZnCl_2(DMA)_2$]	−1 055 ± 5	−84.2 ± 1.6
[$CdCl_2$(DMA)]	−698 ± 2	−29.2 ± 0.2
[$HgCl_2$(DMA)]	−527 ± 2	−24.9 ± 0.3 [a]
		−25.2 ± 0.7 [b]

[a] Ethanol as solvent. [b] 1,2-Dichloroethane as solvent.

DISCUSSION

The melting point, thermogravimetric, and mass spectral results suggest that the adducts do not exist in significant amounts in the gas phase. The value of $\Delta H_R^\ominus$ was determined in dioxan, methanol, and 1,2-dichloroethane or ethanol for zinc, cadmium, and mercury, respectively. The dissociation of metal–ligand adducts in a poorly solvating medium such as 1,2-dichloroethane can be detected by ^1H n.m.r. spectroscopy of the adducts, which showed the unchanged position of the peaks of DMA. By means of the results of Table 1, the enthalpy of the reaction; $HgCl_2$(soln.) + DMA (solvent) $\xrightarrow{\Delta H_i^\ominus}$ [$HgCl_2$(DMA)] (soln.); $\Delta H_i^\ominus = 0.46 \pm 1.31$ kJ mol^{-1}, was calculated. This small value of $\Delta H_i^\ominus$ in 1,2-dichloroethane corroborates with the weak metal–ligand interaction.

It is of great interest to evaluate the enthalpy of the metal–oxygen bond, $\Delta H^\ominus$(M–O), in these adducts. For this purpose consider the reaction in the gas phase: $MCl_2(g) + nDMA(g) \xrightarrow{\Delta H_g^\ominus} [MCl_2(DMA)_n]$ (g), where $\Delta H_g^\ominus = n\Delta H^\ominus$(M–O). Usually, the following thermodynamic cycle can be used for the determination of $\Delta H^\ominus$ (M–O):

$$\begin{tikzcd}
MCl_2(g) & +\, nDMA(g) \arrow[r, "\Delta H_g^\ominus"] & {[MCl_2(DMA)_n](g)} \\
MCl_2(s) \arrow[u, "\Delta H_{sub}^\ominus"] & +\, nDMA(l) \arrow[u, "\Delta H_{vap}^\ominus"] \arrow[r, "\Delta_R H^\ominus"] & {[MCl_2(DMA)_n](s)} \arrow[u, "\Delta H_a^\ominus"]
\end{tikzcd}$$

The enthalpies of sublimation of these adducts, $\Delta H_a^\ominus$, are not experimentally accessible due to thermal decomposition. To get some idea of the relative strengths of the metal–oxygen bonds, it is necessary to make the approximate assumption that the molar enthalpy of sublimation of each adduct is equal to the enthalpy of vaporization of 1 mol of ligand,[25] which is 45.61 kJ mol^{-1} for DMA.[32] The values for $\Delta H^\ominus$(M–O) are then −139, −210, and −106 kJ mol^{-1} for zinc, cadmium, and mercury, respectively. This parallels the order of $\Delta H^\ominus$(M–S) values observed for the thiourea complexes of these metal halides.[24]

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