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Note

THERMOCHEMISTRY OF DIBROMOBIS[*N*-(2-PYRIDYL)ACETAMIDE]ZINC(II) AND -CADMIUM(II), DIIODOBIS[*N*-(2-PYRIDYL)ACETAMIDE]ZINC(II) AND -CADMIUM(II), AND DIBROMO[*N*-(2-PYRIDYL)ACETAMIDE]MERCURY(II)

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The standard enthalpies of formation (kJ mole^{-1}) of Zn(aapH)$_2$Br$_2$ (—702.4 ± 22), Zn(aapH)$_2$I$_2$ (—579.7 ± 22), Cd(aapH)$_2$Br$_2$ (—650.1 ± 22), Cd(aapH)$_2$I$_2$ (—540.7 ± 21) and Hg(aapH)Br$_2$ (—330.0 ± 22), have been determined from the reaction $MX_2(c) + n\ (aapH)\ (c) \rightarrow M(aapH)_nX_2(c)$, which gave the following standard enthalpy changes ($\Delta H_R^{\ominus}$): —76.53 ± 0.83, —74.44 ± 0.75, —36.71 ± 0.78, —40.16 ± 0.42 and —10.66 ± 0.65 kJ mole^{-1}, respectively. Thermochemical results of the reactions $MX_2(g) + n\ (aapH)\ (g) \rightarrow M(aapH)_nX_2(c)$ and $MX_2(c) + n\ (aapH)\ (g) \rightarrow M(aapH)_nX_2(c)$, are also reported.

INTRODUCTION

Previous investigations of adducts of *N*-(2-pyridyl)acetamide with some transition metals [1—3], indicate that the ligand behaves as a bidentate by coordinating the metal simultaneously through the oxygen and the heterocyclic nitrogen. This general bichelating behaviour is changed with the zinc, cadmium and mercury halides. In some adducts, the ligand only uses its heterocyclic nitrogen for coordination [4]. Due to the lack of thermochemical data on the ligand and its compounds, we have recently published the enthalpies of formation and sublimation of the ligand followed by the determination of the enthalpy of formation and other thermochemical data of dichlorobis[*N*-2(pyridyl)acetamide]zinc(II), -cadmium(II) and -mercury(II) [5]. These compounds showed a decrease in the thermochemical values from zinc to mercury and the acidity varies in the sequence ZnCl$_2$ > CdCl$_2$ > HgCl$_2$.

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As part of our interest in continuing the thermochemical study of adducts of aapH and halides of Group IIB, the enthalpies of formation and other thermochemical results of the compounds M(aapH)$_2$X$_2$ (M = Zn, Cd; X = Br, I) and Hg(aapH)Br$_2$ have been determined.

EXPERIMENTAL

Materials

The zinc bromide was prepared by treating zinc with bromine in absolute ether at low temperature [6], the product of this reaction being dried in vacuo. CdBr$_2$ · 4 H$_2$O (E. Merck) was made anhydrous by heating for 10 h in vacuo [7] at 130°C. The pure zinc iodide (E. Merck), cadmium iodide (Carlo Erba) and mercury bromide (Fisher) were dried in vacuo before use. The adducts were prepared and analysed as previously described [4]; however those to be used in the calorimetric determinations, which employ absolute ethanol (E. Merck) as the solvent were recrystallized from ethanol. All compounds were rigorously dried in vacuo before the ampoules to be used in the calorimetry were prepared, and the air sensitive salts were handled in a dry box.

Calorimetric measurements

A calorimetric LKB model 8700-1 was employed for all solution calorimetric determinations. Each measurement was performed at (25.04 ± 0.02)°C, with a thin-walled glass ampoule containing 5—67 mg of the solid reactant being broken in the 100 ml glass reaction vessel which was charged with ethanol. Details of the procedure and the calibration of the calorimeter have been recently reported [8].

Other determinations

The mass spectra of the ligand and the adducts were performed on a Varian-Mat 311A. The thermogravimetric determinations [4] were carried out on a Perkin Elmer thermobalance TGS-1.

RESULTS AND DISCUSSION

The standard enthalpies of formation of the adducts M(aapH)$_n$X$_2$, with $n = 2$ for M = Zn, Cd; X = Br, I and $n = 1$ for M = Hg; X = Br, can be determined from reaction (1) in which ΔH_R^θ gives the difference between the enthalpies of products and reactants in the exact stoichiometries required for reactions (2)—(4) in solution.

$$MX_2(c) + n\ (aapH)(c) \rightarrow M(aapH)_nX_2(c) \qquad (1)$$

$$MX_2(c) + solvent \rightarrow MX_2(soln) \qquad \Delta H_2^{\ominus} \qquad (2)$$

$$MX_2(soln) + n\ (aapH)(c) \rightarrow MX_2(soln) + n\ (aapH)(soln) \qquad \Delta H_3^{\ominus} \qquad (3)$$

$$M(aapH)_2X_2(c) + solvent \rightarrow MX_2(soln) + n\ (aapH)(soln) \qquad \Delta H_4^{\ominus} \qquad (4)$$

Ethanol was selected as a solvent because it easily dissolved the halides, adducts and ligand. To 100 ml of ethanol in a calorimetric vessel [5], ampoules of solid halides and crystalline ligand were added consecutively to produce $\Delta H_2^{\ominus}$ and $\Delta H_3^{\ominus}$. To another equal volume of solvent, ampoules of adducts were broken to give $\Delta H_4^{\ominus}$. In this case the thermodynamically equivalent solution gives $\Delta H_R^{\ominus} = \Delta H_2^{\ominus} + n\Delta H_3^{\ominus} - \Delta H_4^{\ominus}$.

The values of the enthalpies of reactions (2)—(4) are summarized in Table 1. For each calorimetric determination, at least five runs were made. The values of $\Delta H_2^{\ominus}$ indicate that the dissolution of metal halide produces an abrupt change in enthalpy, the exception being mercury chloride which gives a slightly endothermic reaction, whereas the ligand dissolves in this medium to give a practically constant endothermic value ($\Delta H_3^{\ominus}$) and the adduct gives an endothermic value for $\Delta H_4^{\ominus}$. The exothermic value of $\Delta H_R^{\ominus}$ decreases from zinc to mercury for the bromides, even though the latter metal has a different adduct stoichiometry. The same trend is observed for the zinc and cadmium iodide compounds.

The standard enthalpies of formation of the adducts, which are listed in Table 2, can be calculated from eqn. (1), by means of the expression: $\Delta H_{f\,(adduct)}^{\ominus} = \Delta H_R^{\ominus} + n\ \Delta H_{f\,(aapH,c)}^{\ominus} + \Delta H_{f\,(MX_2,c)}^{\ominus}$. The standard enthalpies of the metal halides are available in the literature [9] and that of the ligand was previously obtained by us [5].

The gas phase enthalpies of formation of the adducts may give information about the metal—ligand bond strengths [10]. The adducts do not sublime as was demonstrated by performing thermogravimetry and mass spectrometry at temperatures both above and below the melting point. Only decomposition products were observed [4]. The mass spectra of the free ligand shows *m/z* 136 (aapH), *m/z* 94 (2-aminopyridine), *m/z* 78 (pyridine), and *m/z* 51 (C_4H_3). These same fragments were detected for all adducts and,

TABLE 1

Standard enthalpies for eqns. (2)–(4) and the standard enthalpies of the reactions between the ligand and the respective halides in the solid state

Compound	$\Delta H_2^{\ominus}$ (kJ mole^{-1})	$\Delta H_2^{\ominus}$ (kJ mole^{-1})	$\Delta H_2^{\ominus}$ (kJ mole^{-1})	$\Delta H_2^{\ominus}$ (kJ mole^{-1})
$Zn(aapH_2)Br_2$	−47.69 ± 0.37	20.97 ± 0.16	70.78 ± 0.68	−76.53 ± 0.83
$Zn(aapH)_2I_2$	−52.88 ± 0.35	20.59 ± 0.24	62.74 ± 0.46	−74.44 ± 0.75
$Cd(aapH)_2Br_2$	−5.85 ± 0.05	19.96 ± 0.19	75.85 ± 0.31	−36.71 ± 0.78
$Cd(aapH)_2I_2$	−15.48 ± 0.19	21.21 ± 0.18	67.31 ± 0.43	−40.16 ± 0.42
$Hg(aapH)Br_2$	1.31 ± 0.10	21.59 ± 0.19	33.56 ± 0.61	−10.66 ± 0.65

TABLE 2

Summary of the thermochemical data

Compound	$\Delta H_f^{\ominus}$ (kJ mole^{-1})	$\Delta H_M^{\ominus}$ (kJ mole^{-1})	$\Delta H_L^{\ominus}$ (kJ mole^{-1})
$Zn(aapH)_2Br_2$	−702.4 ± 22	−414	−284
$Zn(aapH)_2I_2$	−579.7 ± 22	−416	−282
$Cd(aapH)_2Br_2$	−650.1 ± 22	−408	−244
$Cd(aapH)_2I_2$	−540.7 ± 21	−394	−248
$Hg(aapH)Br_2$	−330.0 ± 22	−223	−115

in the case of mercury, the peaks of mercury bromide were also observed. The thermograms of the adducts showed a weight loss which is in good agreement with the stoichiometry established for the compounds. The behaviour of decomposition depends on the metal and its stoichiometry as described before [4].

Due to the impossibility of determining the standard enthalpy of formation of the adducts in the gas phase, thermodynamic cycles were employed to calculate data for eqns. (5) and (6), which provide information about the

$$MX_2(g) + n\ (aapH)(g) \rightarrow M(aapH)_nX_2(c) \qquad \Delta H_M^{\ominus} \tag{5}$$

$$MX_2(c) + n\ (aapH)(g) \rightarrow M(aapH)_nX_2(c) \qquad \Delta H_L^{\ominus} \tag{6}$$

interactions of metal halides with ligands [11]. From the enthalphy of formation of the metal halides, its enthalpy of sublimation [12,13] and the enthalpy of sublimation of the ligand, the lattice enthalpy ($\Delta H_M^{\ominus}$) and the inverse of the enthalpy of decomposition ($\Delta H_L^{\ominus}$) were calculated. These results are listed in Table 2, together with the $\Delta H_f^{\ominus}$ of the adducts. These enthalpies decrease from zinc to mercury in the bromide and iodide series, as was observed for the chloride adducts [5]. $\Delta H_L^{\ominus}$ has nearly constant values for halides of the same metal, whereas $\Delta H_f^{\ominus}$ decreases from chloride to iodide within a series of adducts with the same metal.

The standard enthalpy of formation of the adducts in the condensed phase ($\Delta H_R^{\ominus}$) for a given metal decreases with increase in the atomic number of the halides, as was observed for chlorides. These values have been used to relate the donor strength of the ligand [14] in forming isostructural compounds with a fixed acceptor. Although the structures of the adducts are not known, the diminution of $\Delta H_R^{\ominus}$ values from zinc to mercury reflects the decrease in acidity of these metal halides, where *N*-(2-pyridyl)acetamide is the base considered.

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