Thermochemistry of Dichlorobis[*N*-(2-pyridyl)acetamide]-zinc(II), -cadmium(II), and -mercury(II)

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The standard enthalpy changes $\Delta H_R^{\ominus} = -70.80 \pm 0.60$, -35.02 ± 0.72, and -22.90 ± 1.1 kJ mol^{-1} for M = Zn, Cd, and Hg respectively have been measured from the reaction $MCl_2(s) + 2pya(s) \longrightarrow [M(pya)_2]Cl_2(s)$ [pya = *N*-(2-pyridyl)acetamide], by using solution calorimetry. From these values, the standard enthalpy of formation of the ligand ($\Delta H_f^{\ominus} = -149 \pm 21$ kJ mol^{-1}) obtained *via* combustion calorimetry, and literature standard enthalpies of formation of the metal chlorides, the $\Delta H_f^{\ominus}$ values have been determined as -785 ± 22, -724 ± 22, and 544 ± 23 kJ mol^{-1} for M = Zn, Cd, and Hg respectively. The standard enthalpy of sublimation of the ligand (103.8 kJ mol^{-1}) has also been obtained. The standard enthalpies of the reactions $MCl_2(g) + 2pya(g) \longrightarrow [M(pya)_2]Cl_2(c)$ and $MCl_2(c) + 2pya(g) \longrightarrow [M(pya)_2]Cl_2(c)$ have been calculated.

THE ligand *N*-(2-pyridyl)acetamide (pya) has potentially either an oxygen or a heterocyclic nitrogen atom as sites of co-ordination. N.m.r. data suggest that the molecule is planar with deshielding of the H^3 of the pyridine ring by the carbonyl oxygen, suggesting that this group is *trans* to the heterocyclic nitrogen.[1-3] Recent investigations have demonstrated the ability of pya to chelate some transition elements.[3,4] These studies indicate that both the oxygen and the pyridine-nitrogen bond to the metal simultaneously, and consequently an inversion of the carbonyl oxygen is required.[3,4]

In our laboratory we have started a systematic study of Group 2B metals, including the adducts with pya.[5] The interest in these metals stems from the little attention given to them, probably because d^{10} ions are free from crystal-field stabilization energy. The increase in size or polarizability of the metals in the Zn, Cd, Hg triad can reveal interesting features connected with the bonding. For example, in $[Zn(pya)_2]Cl_2$ the organic ligands are bidentate, while in $[Hg(pya)_2]Cl_2$ the ' softer ' metal is co-ordinated only by the heterocyclic nitrogen.[5]

Attempts to study the thermochemistry of the $[M(pya)_2]Cl_2$ adducts have now been made.

EXPERIMENTAL

Materials.—Anhydrous zinc chloride was prepared from the metal and hydrogen chloride in diethyl ether.[6] Cadmium chloride was rendered anhydrous by stirring with acetyl chloride,[7] filtering, and drying *in vacuo*. The anhydrous mercury(II) chloride (Merck) was dried before use. The zinc and cadmium adducts were recrystallized twice from ethanol and the mercury adduct was recrystallized from 1,2-dichloroethane. These adducts were prepared and analyzed as before.[5] Absolute ethanol (Merck) and 1,2-dichloroethane (Carlo Erba) were used as calorimetric solvents. The 1,2-dichloroethane was purified by treating it with potassium hydroxide, drying over calcium chloride, and distilling over P_4O_{10}.

Calorimetry.—We used a conventional static bomb-calorimeter system (Veb Appateban Babelsberg, type Berthelot–Thomsen) similar to that described elsewhere [8] and the usual procedure was followed in order to determine the heat of combustion of pya. The calorimetric bomb of 250 cm^3 internal capacity contained 1 cm^3 of distilled water and the sample of ligand was purged and charged with oxygen up to 30 atm.* After ignition, the amount of reaction was checked from the carbon dioxide collected.[9] The energy equivalent of the calorimeter, $E = -10\,864.5 \pm 20.2$ J K^{-1} where the error quoted is twice the standard deviation of the mean, was determined from the combustion of benzoic acid,[10] which has a specific energy of combustion of $\Delta U = -26\,435.1 \pm 2.9$ J g^{-1}. The correction for nitric acid formation [11] was 59.7 kJ mol^{-1}. To derive $\Delta H_f^{\ominus}$ from $\Delta H_c^{\ominus}$ the following standard enthalpies of formation (kJ mol^{-1}) were used: [12] $\Delta H_f^{\ominus}(H_2O,l) = -(285.83 \pm 0.04)$ and $\Delta H_f^{\ominus}(CO_2,g) = -(393.51 \pm 0.13)$.

The enthalpies of fusion and vaporization and the heat capacities of solid and liquid forms of the ligand were determined in a Perkin-Elmer model DSC-2 differential scanning calorimeter. All the solution calorimetric determinations were carried out in an LKB 8700-1 precision titration calorimeter system. The procedure and calibration have been described.[13] Ampoules containing 3—50 mg of the solid reactant were broken in the 100-cm^3 glass reaction vessel charged with calorimetric solvent and measurements were taken at 25.04 ± 0.2 °C.

RESULTS AND DISCUSSION

The standard enthalpy of the crystalline adducts $[M(pya)_2]Cl_2$ (M = Zn, Cd, or Hg) may be determined from reaction (1) in the solid state.[14] $\Delta H_R^{\ominus}$ represents

$$MCl_2(c) + 2pya(c) \longrightarrow [M(pya)_2]Cl_2(c);\ \Delta H_R^{\ominus} \quad (1)$$

the difference between the enthalpies of the products and reactants when a correct stoicheiometry is considered for the reactions (2)—(4) in solution. To

$$MCl_2(c) + \text{solvent} \longrightarrow MCl_2(\text{soln.});\ \Delta H_2^{\ominus} \quad (2)$$

$$2pya(c) + MCl_2(\text{soln.}) \longrightarrow MCl_2(\text{soln.}) + 2pya(\text{soln.});\ \Delta H_3^{\ominus} \quad (3)$$

$$[M(pya)_2]Cl_2(c) + \text{solvent} \longrightarrow MCl_2(\text{soln.}) + 2pya(\text{soln.});\ \Delta H_4^{\ominus} \quad (4)$$

100.0 cm^3 of solvent in the calorimeter vessel were added ampoules of anhydrous metal halide, prepared in a dry-box, to give $\Delta H_2^{\ominus}$, and addition of the stoicheiometric amount of the ligand to this solution yielded $\Delta H_3^{\ominus}$. Again the calorimeter vessel was charged with the same solvent and ampoules of the adducts were broken to provide numbers of moles of species of the same order as in reaction (2). Thus the thermodynamically equivalent solution gave $\Delta H_R^{\ominus} = \Delta H_2^{\ominus} + 2\Delta H_3^{\ominus} - \Delta H_4^{\ominus}$.

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* Throughout this paper: 1 atm = 101 325 Pa.

The calorimetric solvents were selected for their ability to dissolve the anhydrous halide, the ligand, and the adducts. In all cases at least five runs were made for each calorimetric determination. Table 1 gives the enthalpies of reactions (2)—(4) for a typical example, and Table 2 summarizes the enthalpies for all the adducts. Ethanol was used for the zinc and cadmium reaction series but 1,2-dichloroethane was more convenient for mercury.[13] The change in enthalpy for the metal chloride–solvent interactions ($\Delta H_2^\ominus$), the constant $\Delta H_3^\ominus$, and the small variation of $\Delta H_4^\ominus$ showed that the exothermic enthalpies of $\Delta H_\mathrm{R}^\ominus$ are in the sequence Zn > Cd > Hg.

TABLE 1

Thermodynamic data for reactions (2)—(4) for zinc complexes at 298 K

$10^5\ n(\mathrm{ZnCl_2})$/mol	$Q_\mathrm{obs.}$/J	$10^5\ n(\mathrm{pya})$/mol	$Q_\mathrm{obs.}$/J	$10^5\ n[\mathrm{Zn(pya)_2Cl_2}]$/mol	$Q_\mathrm{obs.}$/J
4.386	−1.672	8.637	1.858	0.8906	0.6977
6.037	−2.451	12.05	2.570	1.796	1.324
7.507	−2.991	15.04	3.173	2.389	1.775
9.385	−3.781	18.71	3.786	3.231	2.321
15.08	−6.176	30.19	6.286	3.671	2.744
20.47	−8.297	41.05	8.457	4.467	3.288
	$\Delta H_2^\ominus = -40.52 \pm 0.21$ kJ mol^{-1}		$\Delta H_3^\ominus = 20.71 \pm 0.12$ kJ mol^{-1}		$\Delta H_4^\ominus = 73.70 \pm 0.51$ kJ mol^{-1}

n = Quantity of substance.

Using the $\Delta H_\mathrm{R}^\ominus$ values [equation (1)] and values of the standard enthalpy of formation of metal chlorides available in the literature,[11] the standard enthalpy of the adduct may be calculated from expression (5). The

$$\Delta H_\mathrm{f}^\ominus(\text{adduct}) = \Delta H_\mathrm{R}^\ominus + 2\Delta H_\mathrm{f}^\ominus(\text{pya,c}) + \Delta H_\mathrm{f}^\ominus(\mathrm{MCl_2,c}) \quad (5)$$

standard enthalpy of the ligand was obtained from the combustion: $\mathrm{C_7H_8N_2O(c)} + 8.5\mathrm{O_2(g)} \longrightarrow 7\mathrm{CO_2(g)} + 4\mathrm{H_2O(l)} + \mathrm{N_2(g)}$. The average enthalpy of combustion per mol, −3 748.1 ± 20 kJ mol^{-1}, was obtained in four runs, and from it can be obtained the standard enthalpy of formation of −149 ± 21 kJ mol^{-1}. Table 3 reports the values of the standard enthalpy of formation of the adducts.

TABLE 2

Standard enthalpies (kJ mol^{-1}) for equations (1)—(4)

$[\mathrm{M(pya)_2}]\mathrm{Cl_2}$	$\Delta H_2^\ominus$	$\Delta H_3^\ominus$	$\Delta H_4^\ominus$	$\Delta H_\mathrm{R}^\ominus$
M = Zn	−40.52 ± 0.21	20.71 ± 0.12	73.40 ± 0.51	−72.80 ± 0.60
Cd	−7.20 ± 0.10	19.86 ± 0.15	67.54 ± 0.87	−35.02 ± 0.72
Hg	13.40 ± 0.30	21.30 ± 0.27	78.90 ± 0.68	−22.90 ± 1.1

TABLE 3

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

$[\mathrm{M(pya)_2}]\mathrm{Cl_2}$	$\Delta H_\mathrm{f}^\ominus$	$\Delta H_\mathrm{M}^\ominus$	$\Delta H_\mathrm{L}^\ominus$
M = Zn	−785 ± 22	−429	−281
Cd	−724 ± 22	−423	−243
Hg	−544 ± 23	−315	−231

The d.s.c. thermograms of the ligand showed fusion as a sharp peak at 343 K which gave $\Delta H_\mathrm{fus.}^\ominus = 16.0$ kJ mol^{-1}, and vaporization as a broad peak at 520 K which gave $\Delta H_\mathrm{vap.} = 37.7$ kJ mol^{-1}. Thus the enthalpy of sublimation can be calculated from $\Delta H_\mathrm{sub.}^\ominus(298\ \mathrm{K}) = \int_{298}^{343} C_p(\mathrm{c})\mathrm{d}T + \Delta H_\mathrm{fus.}^\ominus(343\ \mathrm{K}) + \int_{343}^{520} C_p(\mathrm{l})\mathrm{d}T + \Delta H_\mathrm{vap.}^\ominus(520\ \mathrm{K}) + \int_{298}^{520} C_p(\mathrm{g})\mathrm{d}T$. The values of $C_p(\mathrm{c}) = 3.9 \times 10^2$ J K^{-1} mol^{-1} and $C_p(\mathrm{l}) = 4.2 \times 10^2$ J K^{-1} mol^{-1} were determined, and $C_p(\mathrm{g}) = 1.8 \times 10^2$ J K^{-1} mol^{-1} was estimated by the use of the method of generalized vibrational assignments.[15] Substitution of the known values in the equation above leads to $\Delta H_\mathrm{sub.}^\ominus(298\ \mathrm{K}) = 17.4 + 16.0 + 73.5 + 37.7 - 40.8 = 103.8$ kJ mol^{-1}.

Thermogravimetry of the adducts showed that the compounds decomposed, thus ruling out the possibility of obtaining the gas-phase enthalpies of formation, which could supply information about the metal–ligand bond strength.[16]

To take advantage of the reaction in the solid state, thermodynamic cycles were used to verify the interactions of the metal chloride [11,17,18] with the ligand to give crystals as in equations (6) and (7). Table 3 summarizes the thermochemical data for equations (6)

$$\mathrm{MCl_2(g)} + 2\mathrm{pya(g)} \longrightarrow [\mathrm{M(pya)_2}]\mathrm{Cl_2(c)};\ \Delta H_\mathrm{M}^\ominus \quad (6)$$

$$\mathrm{MCl_2(c)} + 2\mathrm{pya(g)} \longrightarrow [\mathrm{M(pya)_2}]\mathrm{Cl_2(c)};\ \Delta H_\mathrm{L}^\ominus \quad (7)$$

and (7) and the enthalpies of formation of the adducts ($\Delta H_\mathrm{f}^\ominus$), which decrease from zinc to mercury. The same trend is observed for the adduct lattice enthalpies ($\Delta H_\mathrm{M}^\ominus$) and the enthalpies of the reaction shown in equation (7) ($\Delta H_\mathrm{L}^\ominus$), which can be considered as the inverse of the enthalpy of decomposition.[19]

The heats of formation of the complexes in the condensed phase ($\Delta H_\mathrm{R}^\ominus$) have been used to relate the donor strength of the ligands in relation to a fixed acceptor.[20] Considering pya as a fixed donor, although the structures of the adducts are not known, the order $\mathrm{ZnCl_2} > \mathrm{CdCl_2} > \mathrm{HgCl_2}$ might represent the relative acidity in this series of halides.

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