Heterocyclic Nitrogen-containing Electron-pair Donor Ligands: A Thermochemical Study of Adducts with Zinc, Cadmium, and Mercury Chlorides

Claudio Airoldi,* Maria L. C. P. Silva, and Aécio P. Chagas
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13100 Campinas, São Paulo, Brasil

The standard enthalpies ($\Delta H_R^\ominus$/kJ mol^{-1}) of the reactions $MCl_2(s) + nL(s,l) \longrightarrow MCl_2{\cdot}nL(s)$ for ligands pyridine (py), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen) were measured calorimetrically at 298.15 K, giving: $ZnCl_2{\cdot}2py$, −116.1 ± 1.0; $CdCl_2{\cdot}py$, −46.8 ± 0.5; $HgCl_2{\cdot}py$, −43.4 ± 0.4; $ZnCl_2{\cdot}bipy$, −82.9 ± 0.5; $CdCl_2{\cdot}bipy$, −53.9 ± 1.6; $HgCl_2{\cdot}bipy$, −37.7 ± 0.9; $ZnCl_2{\cdot}phen$, −83.5 ± 1.5; $CdCl_2{\cdot}phen$, −61.7 ± 1.7; and $HgCl_2{\cdot}phen$, −60.0 ± 1.6. The standard enthalpy of formation of bipy (216.4 ± 7.4 kJ mol^{-1}) was derived by combustion calorimetry, while that for phen (354 kJ mol^{-1}) was obtained by an estimative calculation method. The standard enthalpies of formation of the adducts were calculated, showing a decrease from zinc to mercury, and for each metal chloride the decrease py > bipy > phen was observed. The standard enthalpies of sublimation of the ligands bipy and phen were calculated, giving 67 and 65 kJ mol^{-1}, respectively. The standard enthalpy of the metal–nitrogen bond, $\bar{D}$(M–N), was calculated by assuming the equivalence of each bond in a bidentate ligand. Values of $\bar{D}$(M–N) for adducts of bidentate ligands were lower than the corresponding ones of pyridine.

Heterocyclic nitrogen-containing electron-pair donor ligands such as pyridine (py), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen) are extensively cited in co-ordination chemistry literature due to their great ability to combine with the majority of metals ions.[1] During this interactive process the ligand electron pair is donated to a metal to form an adduct. Neglecting other features of the complex formed, phen maintains its planarity, while bipy almost always presents a non-planar structure. The co-ordinating characteristics of these ligands are displayed by displacement of the main bands in the i.r. region.[2]

The great majority of publications involving metal complexes of py, bipy, and phen have been directed to the preparation, characterization of the complexes, and related spectroscopic studies. For example, the preparation, properties, and i.r. spectra of the adducts $MCl_2{\cdot}nL$ (L = py, bipy, or phen; M = Zn, Cd, or Hg; n = 1 or 2) have been extensively studied.[3] The same sort of systematic approach has been applied to cationic methylmercury(II) compounds, $[HgMeL][NO_3]$, for all three ligands. In this case, complementary ^1H n.m.r. data suggested that the metal is located in a three-co-ordinated site for the bipy complex in solution.[4]

Some interesting features are related to the structure of mercury adducts. The dimeric form of $HgBr_2{\cdot}bipy$ has been described as having the metal in either a four- or a five-co-ordination site, with the anions in bridging or in terminal positions.[5] On the other hand, $HgCl_2{\cdot}2py$ formed a polymeric one-dimensional array of *trans*-$HgCl_4N_2$ octahedra, sharing two opposite edges, while $HgX_2{\cdot}2py$ (X = Br or I) formed discrete pseudo-tetrahedral molecules.[6]

The ^{13}C n.m.r. spectra of $MCl_2{\cdot}2py$ (M = Zn, Cd, or Hg) compounds suggested a π-cloud delocalization in the ring of the adducts,[7] considerably different from that of the free ligand. ^{113}Cd N.m.r. spectra for $CdX_2{\cdot}2bipy$ (X = Cl or Br) showed two different cationic species, with each metal separated by the van der Waals distance, resulting in a near octahedral co-ordination.[8]

Thermal studies of adducts are scarce. A relevant publication in this field is concerned with the determination of the enthalpy of decomposition of $CoX_2{\cdot}nL$ (n = 2 or 4; X = Cl, Br, or I; L = py, 2-, 3-, or 4-methylpyridine, aniline, or quinoline) by means of a quantitative thermal differential analysis.[9] This study was also extended to pyridine and quinoline first-row transition-metal halide adducts, $MX_2{\cdot}2L$, in which zinc and cadmium were included. Nevertheless, the enthalpy of decomposition for $ZnCl_2{\cdot}2py$ was not obtained.[10]

The acidity properties of mercury halides were reviewed recently.[11] In particular, the thermodynamic data for the formation of 1:1 complexes in benzene solution were reported for mercury chloride interacting with heterocyclic ligands like py, 2-methylpyridine, 4-methylpyridine, or bipy.

In the light of the above and considering the lack of thermochemical data involving adducts of MCl_2 (M = Zn, Cd, or Hg) with the above mentioned ligands, this paper reports some calorimetric studies of the adducts $ZnCl_2{\cdot}2py$, $MCl_2{\cdot}py$ (M = Cd or Hg), $MCl_2{\cdot}bipy$, and $MCl_2{\cdot}phen$ (M = Zn, Cd, or Hg).

Experimental

Reagents.—Pyridine was dried over potassium hydroxide before distilling for use. 2,2′-Bipyridine (Sigma) was recrystallized from anhydrous ethanol. Hemihydrated 1,10-phenanthroline (Carlo Erba) was dehydrated by standing in a desiccator over sulphuric acid for several hours. All solvents for calorimetric determinations were dried according to standard procedures. Anhydrous zinc and cadmium chlorides were prepared as previously described.[12] Mercury chloride (E. Merck) was dried *in vacuo* before use.

Preparation of the Adducts.—These preparations were carried out with pure chemical grade reagents. Operations involving air-sensitive compounds were carried out either *in vacuo* or in a dry-box under an atmosphere of dried nitrogen.[13] All the adducts were prepared similarly. The method for obtaining $CdCl_2{\cdot}py$ illustrates the general procedure.

To a solution of $CdCl_2$ (0.699 g, 3.81 mmol) in ethanol (5.0 cm^3) was added dropwise, with stirring, pyridine (0.355 cm^3,

Table 1. Molar enthalpies of dissolution at 298.15 K; the number is associated with the individual enthalpies used in the calculation $\Delta H_R^\circ = n\Delta H_1^\circ + \Delta H_2^\circ - \Delta H_3^\circ$

Number	Reaction *	ΔH°/kJ mol^{-1}
1	$\mathrm{py(l) + EtOH \longrightarrow py(EtOH)}$	-1.73 ± 0.03
2	$\mathrm{ZnCl_2(s) + 2py(EtOH) \longrightarrow ZnCl_2{\cdot}2py(EtOH)}$	-45.49 ± 0.66
3	$\mathrm{ZnCl_2{\cdot}2py(s) + EtOH \longrightarrow ZnCl_2{\cdot}2py(EtOH)}$	67.13 ± 0.71
1	$\mathrm{py(l) + (HNO_3\ 2\ mol\ dm^{-3}) \longrightarrow py(HNO_3\ 2\ mol\ dm^{-3})}$	-33.07 ± 0.43
2	$\mathrm{CdCl_2(s) + py(HNO_3\ 2\ mol\ dm^{-3}) \longrightarrow CdCl_2{\cdot}py(HNO_3\ 2\ mol\ dm^{-3})}$	-4.29 ± 0.13
3	$\mathrm{CdCl_2{\cdot}py(s) + (HNO_3\ mol\ dm^{-3}) \longrightarrow CdCl_2{\cdot}py(HNO_3\ mol\ dm^{-3})}$	9.40 ± 0.19
1	$\mathrm{py(l) + EtOH \longrightarrow py(EtOH)}$	-1.73 ± 0.03
2	$\mathrm{HgCl_2(s) + py(EtOH) \longrightarrow HgCl_2{\cdot}py(EtOH)}$	-1.27 ± 0.01
3	$\mathrm{HgCl_2{\cdot}py(s) + EtOH \longrightarrow HgCl_2{\cdot}py(EtOH)}$	40.39 ± 0.44
1	$\mathrm{bipy(s) + (MeOH + HCl\ 0.5\ mol\ dm^{-3}) \longrightarrow bipy(MeOH + HCl\ 0.5\ mol\ dm^{-3})}$	-9.93 ± 0.13
2	$\mathrm{ZnCl_2(s) + bipy(MeOH + HCl\ 0.5\ mol\ dm^{-3}) \longrightarrow ZnCl_2{\cdot}bipy(MeOH + HCl\ 0.5\ mol\ dm^{-3})}$	-34.05 ± 0.15
3	$\mathrm{ZnCl_2{\cdot}bipy(s) + (MeOH + HCl\ 0.5\ mol\ dm^{-3}) \longrightarrow ZnCl_2{\cdot}bipy(MeOH + HCl\ 0.5\ mol\ dm^{-3})}$	38.94 ± 0.47
1	$\mathrm{bipy(s) + (1\ NH_2CH_2CH_2OH + 3\ EtOH) \longrightarrow bipy(1\ NH_2CH_2CH_2OH + 3\ EtOH)}$	21.41 ± 0.22
2	$\mathrm{CdCl_2(s) + bipy(1\ NH_2CH_2CH_2OH + 3\ EtOH) \longrightarrow CdCl_2{\cdot}bipy\ (1\ NH_2CH_2CH_2OH + 3\ EtOH)}$	-101.83 ± 1.49
3	$\mathrm{CdCl_2{\cdot}bipy(s) + (1\ NH_2CH_2CH_2OH + 3\ EtOH) \longrightarrow CdCl_2{\cdot}bipy\ (1\ NH_2CH_2CH_2OH + 3\ EtOH)}$	-26.51 ± 0.39
1	$\mathrm{bipy(s) + (MeOH + HNO_3\ 2.5\ mol\ dm^{-3}) \longrightarrow bipy(MeOH + HNO_3\ 2.5\ mol\ dm^{-3})}$	-29.09 ± 0.78
2	$\mathrm{HgCl_2(s) + bipy(MeOH + HNO_3\ 2.5\ mol\ dm^{-3}) \longrightarrow HgCl_2{\cdot}bipy\ (MeOH + HNO_3\ 2.5\ mol\ dm^{-3})}$	11.44 ± 0.29
3	$\mathrm{HgCl_2{\cdot}bipy(s) + (MeOH + HNO_3\ 2.5\ mol\ dm^{-3}) \longrightarrow HgCl_2{\cdot}bipy\ (MeOH + HNO_3\ 2.5\ mol\ dm^{-3})}$	20.09 ± 0.35
1	$\mathrm{phen(s) + (HNO_3\ 2\ mol\ dm^{-3}) \longrightarrow phen(HNO_3\ 2\ mol\ dm^{-3})}$	-20.31 ± 0.32
2	$\mathrm{ZnCl_2(s) + phen(HNO_3\ 2\ mol\ dm^{-3}) \longrightarrow ZnCl_2{\cdot}phen(HNO_3\ mol\ dm^{-3})}$	-55.89 ± 1.50
3	$\mathrm{ZnCl_2{\cdot}phen(s) + (HNO_3\ 2\ mol\ dm^{-3}) \longrightarrow ZnCl_2{\cdot}phen(HNO_3\ 2\ mol\ dm^{-3})}$	7.29 ± 0.10
1	$\mathrm{phen(s) + (1\ NH_2CH_2CH_2OH + 3\ EtOH) \longrightarrow phen(1\ NH_2CH_2CH_2OH + 3\ EtOH)}$	9.61 ± 0.41
2	$\mathrm{CdCl_2(s) + phen(1\ NH_2CH_2CH_2OH + 3\ EtOH) \longrightarrow CdCl_2{\cdot}phen\ (1\ NH_2CH_2CH_2OH + 3\ EtOH)}$	-104.42 ± 1.38
3	$\mathrm{CdCl_2{\cdot}phen(s) + (1\ NH_2CH_2CH_2OH + 3\ EtOH) \longrightarrow CdCl_2{\cdot}phen\ (1\ NH_2CH_2CH_2OH + 3\ EtOH)}$	-33.09 ± 0.80
1	$\mathrm{phen(s) + (1\ NH_2CH_2CH_2OH + 3\ dmso) \longrightarrow phen(1\ NH_2CH_2CH_2OH + 3\ dmso)}$	11.35 ± 0.23
2	$\mathrm{HgCl_2(s) + phen(1\ NH_2CH_2CH_2OH + 3\ dmso) \longrightarrow HgCl_2{\cdot}phen\ (1\ NH_2CH_2CH_2OH + 3\ dmso)}$	-132.13 ± 1.56
3	$\mathrm{HgCl_2{\cdot}phen(s) + (1\ NH_2CH_2CH_2OH + 3\ dmso) \longrightarrow HgCl_2{\cdot}phen\ (1\ NH_2CH_2CH_2OH + 3\ dmso)}$	-60.74 ± 0.16

* dmso = Dimethyl sulphoxide.

12.6 mmol) dissolved in ethanol (5.0 cm^3). A white solid appeared immediately, and the reaction was complete upon ending the addition. The resulting solution was stirred magnetically for a further 2 h. The precipitate was filtered off, washed three times with anhydrous ethanol, and dried *in vacuo* for several hours. Attempts to prepare adducts of different stoicheiometry with the same metal chloride were unsuccessful. Metal[14] or chloride[15] analysis for the zinc and cadmium adducts gave very satisfactory results. For the insoluble adducts of mercury chloride, elemental analyses of carbon, nitrogen, and hydrogen were made.

Calorimetry.—A static calorimetric bomb system (Veb Apparatenban, Babelsberg) was used for the determination of the enthalpy of combustion of bipy, for which the calibration and general procedure have been described before.[12] In all experiments the calorimetric bomb, with 250-cm^3 internal capacity, was charged with 30 atm of oxygen (1 atm = 101 325 Pa). The equivalent energy of the calorimeter $E = 101\,40 \pm 8$ J K^{-1} was determined from the combustion of samples of benzoic acid, for which $\Delta U_c = -(26\,435.1 \pm 2.9)$ J g^{-1}. The following auxiliary data were used: ΔH_f° ($\mathrm{HNO_3}$,l) = -59.7,[16] ΔH_f° ($\mathrm{H_2O}$,l) = $-(285.83 \pm 0.04)$,[17] and ΔH_f° ($\mathrm{CO_2}$,g) = $-(393.51 \pm 0.31)$ kJ mol^{-1}.[17]

The standard enthalpies of fusion, and the heat capacities of bipy and phen have been determined by using a Perkin-Elmer model 2 differential scanning calorimeter. Six individual samples of both ligands were used for the enthalpy determinations, with masses in the range 3—6 mg. The heat capacities of the ligands in their solid and liquid forms were obtained from seven samples each, with masses 3—7 mg. For the heat capacity determinations the constant of calibration, $K = 0.0354$ cm^{-1}, was obtained from seven measurements of the fusion of an indium standard.[18]

The d.s.c. curves show decomposition of bipy and phen without vaporization. From various determinations with different masses the pseudo process of vaporization was observed which gave mean values at 460 and 485 K, respectively. The respective enthalpies of sublimation were estimated by means of Giacolone, Riedel–Planck–Miller, and Watson empirical equations.[19]

A LKB 8700–1 precision calorimetric system was used to determine the enthalpies of dissolution at 298.15 ± 0.02 K of the salts, adducts, and ligands in the appropriate solvent. Previously described criteria for choosing the calorimetric solvent were used.[13,20] For these measurements sealed thin-glass ampoules containing masses in the range 5—60 mg were broken into the vessel charged with 100.0 cm^3 of thermostatted calorimetric solvent.[13,20]

Other Measurements.—Infrared spectra were obtained from samples mulled in Nujol or Fluorolube, using a Perkin-Elmer 180 spectrophotometer. Melting points were determined in a Mettler FP-52 instrument coupled with a Mettler FP-5 recorder. Thermogravimetric curves were obtained by using a Perkin-Elmer model TGS-1 thermobalance with a programmed speed of heating of 5 °C min^{-1} in a dry nitrogen flux.[13]

Results

The adducts are white, non-hygroscopic and melt above 573 K, with the exception of $\mathrm{ZnCl_2{\cdot}2py}$ and $\mathrm{HgCl_2{\cdot}py}$, which appear to fuse at 438—440 and 400—403 K, respectively. From the thermogravimetric curves, one observes a decomposition and not a fusion for both adducts.

The standard enthalpies of the reactions (ΔH_R°) in the condensed phase, $\mathrm{MCl_2(s)} + n\mathrm{L(s,l)} \longrightarrow \mathrm{MCl_2{\cdot}}n\mathrm{L(s)}$, which resulted from the standard enthalpies of reactions 1, 2, and 3, in the appropriate solvent, are listed in Table 1. For each reaction its enthalpy was determined from at least five measurements.

The standard enthalpies of formation of the adducts were

Table 2. Thermochemical results for adducts (kJ mol^{-1})

Substance	$\Delta H_R^\ominus$	$\Delta H_f^{\ominus a}$	$\Delta H_D^\ominus$	$\Delta H_M^{\ominus b}$	$\Delta H_g^{\ominus b}$	$\bar{D}$(M–N)
$ZnCl_2\cdot 2py$	-116.1 ± 1.0	-330.8 ± 1.1	196.5 ± 1.0	-345.5 ± 1.0	-305.3 ± 1.0	153
$ZnCl_2\cdot bipy$	-82.9 ± 0.5	-281.6 ± 7.4	149.9 ± 0.5	-298.9 ± 0.5	-231.9 ± 0.5	116
$ZnCl_2\cdot phen$	-83.5 ± 1.5	-255.2 ± 1.5	148.5 ± 1.5	-297.5 ± 1.5	-232.5 ± 1.5	116
$CdCl_2\cdot py$	-46.8 ± 0.5	-338.1 ± 0.8	87.0 ± 0.5	-268.2 ± 0.5	-228.0 ± 0.5	228
$CdCl_2\cdot bipy$	-53.9 ± 1.6	-229.0 ± 7.6	120.9 ± 1.6	-302.1 ± 1.6	-235.1 ± 1.6	118
$CdCl_2\cdot phen$	-61.7 ± 1.7	-209.8 ± 1.7	126.7 ± 1.7	-307.9 ± 1.7	-242.9 ± 1.7	121
$HgCl_2\cdot py$	-43.4 ± 0.4	-167.5 ± 0.7	83.6 ± 1.4	-166.4 ± 0.4	-126.2 ± 0.4	126
$HgCl_2\cdot bipy$	-37.7 ± 0.9	-45.6 ± 7.5	104.7 ± 0.9	-187.5 ± 0.9	-120.5 ± 0.9	60
$HgCl_2\cdot phen$	-60.0 ± 1.6	-40.9 ± 1.6	125.0 ± 1.6	-207.8 ± 1.6	-142.8 ± 1.6	71

[a] $\Delta H_f^\ominus$ (MCl_2, s) [M = Zn(-415.1 ± 0.03), Cd(-391.5 ± 0.3), or Hg(-224.3 ± 0.2); $\Delta H_{sub}^\ominus(ZnCl_2)$ = 149 kJ mol^{-1}] were quoted from ref. 21. [b] $\Delta H_{sub}^\ominus$ (MCl_2) [M = Cd(181.2 ± 0.1) or Hg(82.8 ± 0.02) kJ mol^{-1}] were taken from F. J. Keneshea and D. Cubicciotti, *J. Chem. Phys.*, 1964, **40**, 1778 and L. G. Hepler and G. Olofsson, *Chem. Rev.*, 1975, **75**, 588, respectively.

Table 3. The main i.r. stretching (ν) and bending (δ) bands (cm^{-1}) for ligands and adducts

Compound	δ(C–H)		ν(C=C)	ν(C=N)
py	1 130	740	1 580	1 450
bipy	1 140	752	1 579	1 450
phen	1 140	748	1 588	1 460
$ZnCl_2\cdot 2py$	1 160	760	1 600	1 460
$CdCl_2\cdot py$	1 152	750	1 588	1 460
$HgCl_2\cdot py$	1 160	750	1 550	1 460
$ZnCl_2\cdot bipy$	1 155	770	1 595	1 465
$CdCl_2\cdot bipy$	1 154	772	1 590	1 460
$HgCl_2\cdot bipy$	1 160	765	1 580	1 440
$ZnCl_2\cdot phen$	1 222	780	1 582	1 460
$CdCl_2\cdot phen$	1 224	775	1 580	1 460
$HgCl_2\cdot phen$	1 222	772	1 575	1 460

calculated by using $\Delta H_R^\ominus$ values, the standard enthalpies of formation of the metal chlorides, which are $-(415.1 \pm 0.03)$, $-(391.5 \pm 0.3)$, and $-(224.3 \pm 0.2)$ kJ mol^{-1} for zinc, cadmium, and mercury,[21] respectively, and the enthalpies of formation of the ligands, *i.e.*, $\Delta H_f^\ominus(\text{adduct, s}) = \Delta H_f^\ominus(MCl_2,s) + n\Delta H_f^\ominus(L,s,l) + \Delta H_R^\ominus$. For pyridine[22] $\Delta H_f^\ominus$ and $\Delta H_{sub}^\ominus$ are 100.2 ± 0.5 and 40.2 ± 0.04 kJ mol^{-1}, respectively. The standard enthalpy of formation of bipy in the solid state was derived from its enthalpy of combustion: $C_{10}H_8N_2(s) + 12\ O_2(g) \longrightarrow 10\ CO_2(g) + 4\ H_2O(l) + N_2(g)$; $\Delta H_c^\ominus = -(5\,294.8 \pm 7.3)$ kJ mol^{-1}. This value of $\Delta H_c^\ominus$ resulted from six determinations, giving $\Delta H_f^\ominus(\text{bipy, s}) = 216.4 \pm 7.4$ kJ mol^{-1}. The error quoted is twice the standard deviation of the mean and included all the uncertainties of the auxiliary data used.

The d.s.c. thermograms for bipy and phen showed sharp peaks at 342 and 398 K respectively, from which were calculated the enthalpies of fusion, 19.9 ± 0.2 and 15.0 ± 0.3 kJ mol^{-1}, respectively. The mean standard enthalpies of vaporization, calculated by using empirical methods, were 41.55 ± 0.33 and 43.89 ± 0.35 kJ mol^{-1}, respectively.

The heat capacities of bipy and phen in their solid and liquid forms were also determined, giving $C_p(s) = 0.21$ and $C_p(l) = 0.23$ kJ K^{-1} mol^{-1}, and $C_p(s) = 0.29$ and $C_p(l) = 9.23$ kJ K^{-1} mol^{-1}, respectively. The heat capacities in the gas phase were estimated by means of the method of generalized vibrational assignment[19] through the expressions $C_p(\text{bipy,g}) = -6.95 \times 10^{-2} + 8.77 \times 10^{-4}\ T - 4.50 \times 10^{-7}\ T^2$ and $C_p(\text{phen,g}) = -7.06 \times 10^{-2} + 9.37 \times 10^{-4}\ T - 4.89 \times 10^{-7}\ T^2$.

By using all these data, the enthalpy of sublimation can be calculated by the expression (1), which gave values of 67 and 65 kJ mol^{-1} for bipy and phen respectively.

In the case of phen, its standard enthalpy of formation in the gaseous phase (419 kJ mol^{-1}) has previously been estimated by means of Benson's method.[23] However some enthalpy group

$$\Delta H_{sub}^\ominus\ (298\text{ K}) = \int_{298}^{T_{fus}} C_p(s)dT + \Delta H_{fus}^\ominus\ (T_{fus}) + \int_{T_{fus}}^{T_{vap}} C_p(l)dT + \Delta H_{vap}^\ominus\ (T_{vap}) - \int_{298}^{T_{vap}} C_p(g)dT \qquad (1)$$

contributions required are not properly quoted in the literature, thus $\Delta H_f^\ominus$(phen, g) was estimated by following a referee's suggestion. This procedure considers the molecules in the gaseous phase, where the difference in enthalpies between biphenyl[22] and bipy, 182.1 ± 2.5 and 283.4 ± 7.4 kJ mol^{-1}, respectively, is the same as that between phenanthrene[22] (207.1 ± 4.6 kJ mol^{-1}) and phen. From this asumption $\Delta H_f^\ominus$(phen, g) = 308.4 kJ mol^{-1}) and from which $\Delta H_f^\ominus$ (phen, s) = 243.4 kJ mol^{-1}.

The standard enthalpies of decomposition ($\Delta H_D^\ominus$) of the adducts, $MCl_2\cdot nL(s) \longrightarrow MCl_2(s) + nL(g)$, and the standard enthalpy of formation ($\Delta H_M^\ominus$) of the adducts from reagents in the gas phase, $MCl_2(g) + nL(g) \longrightarrow MCl_2\cdot nL(s)$, were calculated and are listed in Table 2.

An inspection of the i.r. spectra of the adducts, in comparison with the spectra of the free ligands, suggests that the ligands are co-ordinated to the metal by their heteroatom, the stretching C=C and C=N and the bending C–H frequencies undergoing appropriate shifts (Table 3).

Discussion

The thermogravimetric data indicate that the adducts are thermolabile and probably do not exist in appreciable amounts in the gas phase.

The main stretching frequencies C=C and C=N for the ligands are shifted to higher frequencies. However, an opposite shift was shown for C–H in-plane and out-of-plane bending frequencies, Table 3. This behaviour, observed for all the adducts, is in agreement with the mode of co-ordination of the metal to the nitrogen of the heterocyclic molecules.[3]

From the enthalpies of dissolution of the ligands ($\Delta H_1^\ominus$), metal halides ($\Delta H_2^\ominus$), and adducts ($\Delta H_3^\ominus$) given in Table 1, one can obtain the standard enthalpy of the acid–base reaction in the condensed phase ($\Delta H_R^\ominus$). These results are listed in Table 2.

The enthalpy of the reaction $MCl_2(s) + nL(s,l) \longrightarrow MCl_2\cdot nL(s)$, $\Delta H_R^\ominus$, can be used to establish the donor strength of the ligand toward specific acceptors.[13,24] In this case $\Delta H_R^\ominus$ values reflect the Lewis acidities of the zinc family halides. The acid–base strength results from comparison of adducts of the same stoicheiometry, in which crystal enthalpies, reorganization enthalpies, *etc.*, are assumed to be the same. Although $\Delta H_R^{\ominus}$ for the adduct of mercury with phen (-60.04 ± 1.6 kJ mol^{-1}), is slightly smaller than for the corresponding adduct of cadmium (-61.7 ± 1.7 kJ mol^{-1}), the magnitude of $\Delta H_R^{\ominus}$ decreases from zinc to mercury. Consequently, the acidity order for these halides is $ZnCl_2 > CdCl_2 > HgCl_2$. In comparing the relative basicity, phen behaves much more as a base than does bipy with the mercury and cadmium chlorides. However with adducts of zinc the differences in this property are not distinguishable, due to the proximity of the $\Delta H_R^{\ominus}$ values. For py, the acidity order is $CdCl_2 > HgCl_2$. On the other hand, if one considers two py bonds to be equivalent to one bidentate ligand, taking into account the adducts of zinc, the basicity order is py > phen $\simeq$ bipy.

The standard enthalpies of formation of the adducts for each metal–chloride decrease in the order py > bipy > phen. With the exception of the adducts of pyridine, all the $\Delta H_f^{\ominus}$ values decrease from zinc to mercury; such results are shown in Table 2.

The parameter involved in the decomposition of the adducts ($\Delta H_D^{\ominus}$) reflects the variation in enthalpy due to the breakage of metal–ligand bonds and to the rearrangement of the structure of the metal–chloride in returning to its original form. At the same time, $\Delta H_M^{\ominus}$ is related to the metal–ligand interaction and reflects other interactive factors which are linked to the formation of the adducts.[12,13] These parameters were calculated through thermochemical cycles by means of the standard enthalpy of sublimation of the metal chlorides,[21] py,[22] bipy, and phen. Both parameters are useful to compare and systematize adducts,[12,13] these values are listed in Table 2, showing the trends in variation, which are very close to the enthalpies of formation of the adducts.

From the point of view of structural features, there is no doubt about the co-ordination of the ligands to the metals *via* the nitrogen atoms. Thus, in considering the thermochemical context it is important to reiterate that these arguments relate to the metal–nitrogen bond. The enthalpy pertinent to this bond arises from the enthalpy of the reaction ($\Delta H_g^{\ominus}$) in the gas phase, $MCl_2(g) + nL(g) \longrightarrow MCl_2{\cdot}nL(g)$, which can be calculated by means of a thermochemical cycle, where $\bar{D}(M\text{–}N) = \Delta H_g^{\ominus}/n$.

The experimental results show evidence that the adducts decompose on heating, therefore, their enthalpies of sublimation are not experimentally accessible. However, in such a way the enthalpy of the metal–nitrogen bond can be estimated by assuming that the enthalpy of sublimation of the adduct is approximately equal to the enthalpy of vaporization of 1 mol of py or sublimation, in the case of bipy or phen.[13,14,25] Values of $\Delta H_g^{\ominus}$ and $\bar{D}(M\text{–}N)$ are given in Table 2. The first parameter follows the same trend in variation as $\Delta H_R^{\ominus}$ and $\Delta H_f^{\ominus}$. The enthalpy of the metal-nitrogen bond in Table 2 is listed for an individual bond. In this case, the equivalence of each bond in a bidentate ligand was assumed. Then, $\bar{D}(M\text{–}N)$ was equal to half of $\Delta H_g^{\ominus}$. This assumption enables us to compare $\bar{D}(M\text{–}N)$ within the series. As was previously observed,[12,13] the mono adduct $CdCl_2{\cdot}py$ has a higher $\bar{D}(M\text{–}N)$ than the bis adduct $ZnCl_2{\cdot}2py$, which gave 228 and 153 kJ mol^{-1}, respectively. This last value is still higher than those obtained for bidentate ligands, *i.e.*, $ZnCl_2{\cdot}$bipy (116 kJ mol^{-1}) and $ZnCl_2{\cdot}$phen (116 kJ mol^{-1}).

In conclusion, pyridine showed a stronger tendency toward bonding, in comparison with the equivalent behaviour of the other ligands, in relation to the metal chlorides of the zinc family.

Acknowledgements

We thank the CNPq for a fellowship (to M. L. C. P. S.) and FINEP for partial financial support. A referee is also acknowledged for his suggestion in estimating $\Delta H_f^{\ominus}$ (phen, g).

References

1 N. M. Karayannis, A. N. Speca, D. E. Chasan, and L. L. Pytlewsky, *Coord. Chem. Rev.*, 1967, **20**, 37 and refs. therein.
2 J. E. Rüede and D. A. Thornton, *J. Mol. Struct.*, 1976, **34**, 75.
3 S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, 1970, **4**, 291; I. S. Ahuja and P. Rastogi, *J. Chem. Soc. A*, 1970, 2161; A. Syamal, *J. Indian Chem. Soc.*, 1968, **45**, 343; C. Postmus, J. R. Ferraro, and W. Wozniak, *Inorg. Chem.*, 1967, **6**, 2030.
4 A. J. Canty and A. Marker, *Inorg. Chem.*, 1976, **15**, 425.
5 D. C. Craig, Y. Farhangi, D. P. Graddon, and N. C. Stephenson, *Cryst. Struct. Commun.*, 1973, **3**, 155.
6 A. J. Canty, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 15.
7 X. Han, D. Ji, G. Cheng, Z. Fang, and J. Hu, *Kexue Tongbao*, 1981, **26**, 1297; *Chem. Abstr.*, 1982, **96**, 134613.
8 P. F. Rodesiler, R. W. Turner, N. G. Charles, E. A. H. Griffith, and E. L. Amma, *Inorg. Chem.*, 1984, **23**, 999.
9 G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc. A*, 1967, 925.
10 G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc. A*, 1969, 512.
11 D. P. Graddon, *Rev. Inorg. Chem.*, 1982, **4**, 211.
12 C. Airoldi, A. P. Chagas, and F. P. Assunção, *J. Chem. Soc., Dalton Trans.*, 1980, 1823.
13 O. A. Oliveira, A. P. Chagas, and C. Airoldi, *Inorg. Chem.*, 1983, **22**, 136.
14 B. Zak, W. M. Hindman, and E. S. Baginski, *Anal. Chem.*, 1956, **28**, 1661; J. A. Hunter and C. C. Miller, *Analyst* (*London*), 1956, **81**, 79.
15 A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, Green and Co., London, 1961.
16 M. Colomina, P. Jiménez, M. V. Roux, and C. Turrión, *J. Chem. Thermodyn.*, 1978, **10**, 661.
17 CODATA, *J. Chem. Thermodyn.*, 1972, **4**, 331.
18 M. J. O'Neil, *Anal. Chem.*, 1966, **38**, 1331; W. W. Wendlandt, 'Thermal Methods of Analysis,' John Wiley and Sons, New York, 1974.
19 R. C. Reid and T. K. Sherwood, 'The Properties of Gases and Liquids,' 2nd edn., McGraw Hill, New York, 1966; G. J. Janz, 'Thermodynamic Properties of Organic Compounds,' Academic Press, New York, 1968.
20 C. Airoldi, *J. Chem. Soc., Dalton Trans.*, 1985, 369.
21 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schum, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, 1982, **11**, Suppl. 2.
22 J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970.
23 S. W. Benson, 'Thermochemical Kinetics,' 2nd edn., John Wiley and Sons, New York, 1976; S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
24 J. Wilson and I. J. Worral, *J. Chem. Soc. A*, 1967, 392; C. Airoldi, *Inorg. Chem.*, 1981, **20**, 998.
25 S. J. Ashcroft, *J. Chem. Soc. A*, 1970, 1020; R. A. Jorge, C. Airoldi, and A. P. Chagas, *J. Chem. Soc., Dalton Trans.*, 1978, 1102.

Received 23*rd September* 1985; *Paper* 5/1637