Heterocyclic *N*-Oxide Ligands: A Thermochemical Study of Adducts with Zinc, Cadmium, and Mercury Chlorides

Maria L. C. P. da Silva, Aécio P. Chagas, and Claudio Airoldi *
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081 Campinas, São Paulo, Brasil

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The standard enthalpy ($\Delta H_R^{\ominus}$/kJ mol^{-1}) of the reaction $MCl_2(s) + nL(s) \longrightarrow MCl_2{\cdot}nL(s)$ has been determined by solution calorimetry at 298.15 K, for L = pyridine *N*-oxide (pyo) and 2,2′-bipyridine *N,N′*-dioxide (bipyo) and M = Zn, Cd, and Hg: $ZnCl_2{\cdot}2pyo$, −72.1 ± 1.4; $CdCl_2{\cdot}pyo$, −24.7 ± 0.8; $HgCl_2{\cdot}pyo$, −25.7 ± 0.5; $ZnCl_2{\cdot}1.5bipyo$, −105.8 ± 1.0; $CdCl_2{\cdot}bipyo$, −24.0 ± 1.0; and $HgCl_2{\cdot}bipyo$, −4.5 ± 0.4. The standard enthalpies of formation of pyo (7.7 ± 0.8) and bipyo (16.6 ± 5.2 kJ mol^{-1}) were obtained by solution-reaction calorimetry. The standard enthalpy of formation of the adducts decreases from zinc to mercury for both series of compounds. The enthalpy of sublimation of pyo (81.9 ± 1.5 kJ mol^{-1}) was determined from vapour pressure measurements and that of bipyo (180 ± 10 kJ mol^{-1}) was estimated. The mean standard enthalpies of the metal–oxygen bond were also calculated. The results show that pyo is a better ligand for these metal chlorides than is bipyo.

Aromatic heterocyclic *N*-oxide molecules have been used as Lewis bases in co-ordination chemistry due to their great ability of co-ordinating with metals, protons, halogens, and organic electron-pair acceptors.[1] The chemical properties of this class of compounds are related to the presence of the N^+–O^- group, which is polarised such that bonding occurs with metallic ions through the oxygen atom.[1–4] An indication of this mode of co-ordination is shown in shifts in the characteristic bands of the ligands in the i.r. spectra, these being the stretching and bending frequencies of the N–O bond at 1 300—1 200 and 880—830 cm^{-1}, respectively. The observed shift of the first to lower frequencies by 30—40 cm^{-1}, and a slight decrease in frequency for the second band indicate the decrease of N–O bond order on co-ordination.[5]

A great number of publications concerned with synthesis and characterization of aromatic heterocyclic *N*-oxide ligands with metals have appeared, with the ligands bound in an unidentate way, resulting in oxo complexes. More recently, metallic complexes were isolated showing dioxo type bonding.[1–4]

Adducts of zinc, cadmium and mercury chlorides with pyridine *N*-oxide (pyo) and 2,2′-bipyridine *N,N′*-dioxide (bipyo) have been well characterized by vibrational spectroscopy.[6] An *X*-ray diffraction study of $HgCl_2{\cdot}pyo$ showed the ligand bridging the mercury atoms, which are located in a pseudo-octahedral site.[7] Here we present thermochemical data for the adducts of metal chlorides of the zinc group elements with pyo and bipyo, and discuss their thermal behaviour.

Experimental

Reagents.—Pyridine *N*-oxide and 2,2′-bipyridine *N,N′*-dioxide were synthesized as described in the literature.[8,9] Ethanol for calorimetric measurements was dried before use. Zinc(II) and cadmium(II) chlorides were prepared as before.[10] Mercury(II) chloride (E. Merck) was used without further purification.

Preparations.—The adducts were prepared following a general procedure,[9] as illustrated for $CdCl_2{\cdot}bipyo$. To a warmed ethanolic solution of $CdCl_2$ (0.486 g, 2.66 mmol) under magnetic stirring, a warmed ethanolic solution (5.0 cm^3) of bipyo (0.50 g, 2.66 mmol) was added dropwise. A white solid separated immediately. After addition of all the liquid, the solution was stirred for at least 3 h to ensure complete compound formation. The solid was filtered off, washed with ethanol, and dried for several hours.

Analysis for the metals and chloride was carried out by titration as described before.[11]

Calorimetry.—All reaction and solution enthalpies were measured in an isoperibolic precision calorimetric system LKB 8700-1. Samples containing 5—100 mg, sealed in thin glass ampoules, were broken into 100.0 cm^3 of an appropriate thermostatted calorimetric solvent at 298.15 ± 0.02 K. Details of measurement, procedure, apparatus, and data processing have been described previously.[12]

Physical Measurements.—The melting points were obtained in a Mettler FP-52 instrument;[12] for pyo, which is hygroscopic, a sealed capillary was used.[13] Infrared spectra were obtained on Nujol or Fluorolube mulls, using a Perkin-Elmer model 180 spectrophotometer. A Finnigan 1015 S/L spectrometer was used to obtain mass spectra of ligands and adducts. Thermogravimetric (t.g.) curves were obtained using a Perkin-Elmer model TGS-1 thermobalance at a heating rate of 5 °C min^{-1} in a dry nitrogen flux.[12] Conductance measurements were carried out with millimolar concentrations of $ZnCl_2{\cdot}1.5bipyo$ in nitromethane using a Metrohm E 365 Conductoscope bridge operated at 298.15 ± 0.10 K.[14]

Results and Discussion

All the adducts [(melting point, K): $ZnCl_2{\cdot}2pyo$ (433—434), $CdCl_2{\cdot}pyo$ (>573), $HgCl_2{\cdot}pyo$ (438—439), $ZnCl_2{\cdot}1.5bipyo$ (522—523), $CdCl_2{\cdot}bipyo$ (>573), and $HgCl_2{\cdot}bipyo$ (504—505)] are non-hygroscopic and colourless. For all adducts metal and chloride contents were determined to be in complete agreement with the proposed stoicheiometry. For the new adduct, $ZnCl_2{\cdot}1.5bipyo$ (Found: Cl, 16.7; N, 10.0; Zn, 15.5. Calc. for $C_{15}H_{12}Cl_2N_3O_3Zn$: Cl, 16.95; N, 10.05; Zn, 15.6%). Its low conductance (Λ_M = 10.5 ohm^{-1} cm^2 mol^{-1}) in nitromethane is consistent with the existence of non-ionic species in solution.[15] The t.g. data indicated that, with the exception of $ZnCl_2{\cdot}2pyo$, all adducts decompose without fusing, and the recorded mass loss confirms their stoicheiometry. The mass spectra did not show the adduct parent ion, only ligand fragmentation. This is illustrated for bipyo ($C_{10}H_8N_2O_2$): *m/e* 188 ($C_{10}H_8N_2O_2$), 171

Table 1. Molar enthalpies of dissolution in EtOH or EtOH–HCl (1.0 mol dm^{-3}) at 298.15 K

Compound	Calorimetric solvent	No. of experiments	Number (i)*	ΔH_i°/kJ mol^{-1}
pyo(c)	EtOH	5	1	13.23 ± 0.21
$ZnCl_2$(c)	pyo–EtOH	5	2	−40.23 ± 0.79
$ZnCl_2$·2pyo(c)	EtOH	6	3	58.37 ± 1.05
pyo(c)	EtOH–HCl	4	1	6.35 ± 0.17
$CdCl_2$(c)	pyo–EtOH–HCl	6	2	−10.91 ± 0.04
$CdCl_2$·pyo(c)	EtOH–HCl	4	3	41.94 ± 0.83
pyo(c)	EtOH	5	1	13.23 ± 0.21
$HgCl_2$(c)	pyo–EtOH	4	2	0.33 ± 0.01
$HgCl_2$·pyo(c)	EtOH	5	3	39.21 ± 0.46
bipyo(c)	EtOH–HCl	5	1	20.71 ± 0.35
$ZnCl_2$(c)	bipyo–EtOH–HCl	4	2	−28.73 ± 0.36
$ZnCl_2$·1.5bipyo(c)	EtOH–HCl	4	3	108.10 ± 0.85
bipyo(c)	EtOH–HCl	5	1	20.71 ± 0.35
$CdCl_2$(c)	bipyo–EtOH–HCl	4	2	12.89 ± 0.27
$CdCl_2$·bipyo(c)	EtOH–HCl	4	3	57.59 ± 0.89
bipyo(c)	EtOH–HCl	5	1	20.71 ± 0.35
$HgCl_2$(c)	bipyo–EtOH–HCl	4	2	2.29 ± 0.01
$HgCl_2$·bipyo(c)	EtOH–HCl	4	3	27.47 ± 0.21

* Associated with the individual enthalpies (subscripts) used in the calculation $\Delta H_R^{\circ} = n\Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ}$.

Table 2. Auxiliary data (kJ mol^{-1})

Compound	ΔH_f°	$\Delta H_c^{g\circ}$
$ZnCl_2$(c)	−415.1 ± 0.1[a]	149 ± 1.0[a]
$CdCl_2$(c)	−391.5 ± 0.1[a]	180.8 ± 2.1[b]
$HgCl_2$(c)	−224.3 ± 1.0[a]	82.8 ± 1.0[c]
KCl(c)	−436.75 ± 0.01[a]	—
KBr(c)	−393.80 ± 0.01[a]	—
$KClO_3$(c)	−397.7 ± 0.1[a]	—
$KBrO_3$(c)	−360.2 ± 0.1[a]	—
py(l)	100.2 ± 0.7[d]	40.2 ± 0.0[d]
bipy(c)	216.4 ± 7.4[e]	81.93 ± 0.33[f]

[a] Ref. 18 (uncertainties were estimated according to *d*). [b] F. J. Keneshea and D. D. Cubicciotti, *J. Chem. Phys.*, 1964, **40**, 1778. [c] L. G. Hepler and G. Olofsson, *Chem. Rev.*, 1975, **75**, 585. [d] J. B. Pedley, R. D. Naylor, and S. P. Kirby, 'Thermochemical Data of Organic Compounds,' 2nd edn., Chapman and Hall, 1977. [e] Ref. 12. [f] Ref. 19.

($C_{10}H_7N_2O$), 143 ($C_9H_7N_2$), 116 (C_8H_6N), 78 (C_5H_4N), 51 (C_4H_3), and 43 (CNOH). However, for the adduct $HgCl_2$·bipyo, additional peaks were observed corresponding to the decomposition of the salt: *m/e* 270 ($HgCl_2$), 235 (HgCl), 200 (Hg), and 35 (Cl).

The i.r. spectra of pyo showed a very strong band at 1 243 cm^{-1}, attributed to the N–O stretching frequency, which decreased to 1 200 cm^{-1} upon complexation. For bipyo a corresponding doublet at 1 262 and 1 255 cm^{-1} was observed, which persists in the spectra of all adducts, but with a reduction of 30 cm^{-1} in frequency. The strong N–O bending at 842 cm^{-1} in free pyo molecule is shifted 5 cm^{-1} to lower frequency on co-ordination. The shape of the strong doublet at 852 and 840 cm^{-1} for the free bipyo remains in all adducts, however a shift of 7 cm^{-1} to low frequency was observed. These observations are consistent with co-ordination through the oxygen atoms.[1,2,5,6]

The standard molar enthalpies (ΔH_R°) of the following reaction occurring in the condensed phase: $MCl_2(c) + nL(c) \longrightarrow MCl_2{\cdot}nL(c)$ (L = pyo or bipyo) for all adducts, were obtained through the reactions 1, 2, and 3 (Table 1) by using the appropriate calorimetric solvent; ΔH_R° values are useful to compare the acidity of the metals and the basicity of the ligands for adducts of the same stoicheiometry.[11–13] For bipyo the acidity order $CdCl_2 > HgCl_2$ was observed. For pyo the acidity of $CdCl_2$ is very close to that of $HgCl_2$.

The standard molar enthalpies of formation of the adducts were determined using ΔH_R° values, the standard molar enthalpies of formation of metal chlorides (Table 2), and the standard molar enthalpies of the ligands in the solid phase.

The standard molar enthalpies of formation of pyo and bipyo were determined from solution-reaction calorimetry. These determinations were based on the ability of titanium(III) to reduce heterocyclic amine *N*-oxides.[16] For each reaction shown below, the standard molar enthalpy in the condensed phase for

$$KCl(c) + 3\,pyo(c) \longrightarrow KClO_3(c) + 3\,py(l); \quad \Delta H_{r_1}^{\circ}$$

$$KBr(c) + 3\,pyo(c) \longrightarrow KBrO_3(c) + 3\,py(l); \quad \Delta H_{r_2}^{\circ}$$

pyo in $TiCl_3$–HCl solution as calorimetric solvent were 314.02 ± 2.43 and 313.47 ± 2.97 kJ mol^{-1}, respectively. From these values, the standard molar enthalpies of formation were calculated using the standard molar enthalpies of formation listed in Table 2. These data yield values for ΔH_f° (pyo,c) of 8.5 ± 1.1 and 6.9 ± 1.2 kJ mol^{-1} respectively. A mean value of 7.7 ± 0.8 kJ mol^{-1} was used in further calculations.

The same procedure was extended to bipyo; the reactions studied are shown below. Standard molar enthalpies in the con-

$$2\,KCl(c) + 3\,bipyo(c) \longrightarrow 2\,KClO_3(c) + 3\,bipy(c); \quad \Delta H_{r_3}^{\circ}$$

$$2\,KBr(c) + 3\,bipyo(c) \longrightarrow 2\,KBrO_3(c) + 3\,bipy(c); \quad \Delta H_{r_4}^{\circ}$$

densed phase were 671.36 ± 1.16 and 672.78 ± 0.80 kJ mol^{-1}, respectively. Similarly the values obtained for the standard molar enthalpy of formation of bipyo were 18.6 ± 7.4 and 14.5 ± 7.4 kJ mol^{-1}, respectively; the mean value (16.6 ± 5.2 kJ mol^{-1}) was adopted for further calculations.

The enthalpy of sublimation of pyo, 81.9 ± 1.5 kJ mol^{-1}, was determined through the measurement of vapour pressure at various temperatures using a Knudsen effusion cell.[17] Combination of these data allows calculation of the standard molar enthalpy of formation of pyo in the gas phase as ΔH_f° (pyo,g) = 89.6 ± 1.7 kJ mol^{-1}. Attempts to determine the enthalpy of sublimation of bipyo were unsuccessful, due to its very low vapour pressure.[17] This value was calculated starting

Table 3. Summary of the thermochemical results for ligands and adducts (kJ $\mathrm{mol^{-1}}$)

Compound	$\Delta H_R^\ominus$	$\Delta H_f^\ominus$	$\Delta H_D^\ominus$	$\Delta H_M^\ominus$	$\Delta H_g^\ominus$	$\bar{D}$(M–O)
pyo		7.7 ± 0.8				
bipyo		16.6 ± 5.2				
$ZnCl_2 \cdot 2pyo$	−72.1 ± 1.4	−471.8 ± 2.1	235.9 ± 3.3	384.9 ± 3.4	303.0 ± 3.7	151.5 ± 1.9
$CdCl_2 \cdot 2pyo$	−24.7 ± 0.8	−408.5 ± 1.1	106.6 ± 1.7	287.4 ± 2.7	205.5 ± 3.1	205.5 ± 3.1
$HgCl_2 \cdot pyo$	−25.7 ± 0.5	−242.3 ± 1.4	107.6 ± 1.6	190.4 ± 1.9	108.5 ± 2.4	108.5 ± 2.4
$ZnCl_2 \cdot 1.5bipyo$	−105.8 ± 1.0	−496.0 ± 8.0	376 ± 15	525 ± 15	345 ± 18	115 ± 6
$CdCl_2 \cdot bipyo$	−24.0 ± 1.0	−398.9 ± 5.3	204 ± 10	385 ± 10	205 ± 14	103 ± 7
$HgCl_2 \cdot bipyo$	−4.5 ± 0.4	−212.2 ± 5.3	185 ± 10	268 ± 10	88 ± 14	44 ± 7

from the mean standard enthalpy of the N–O bond in pyo based on the decomposition shown below, using the standard molar

$$\mathrm{pyo(g)} \longrightarrow \mathrm{py(g)} + \mathrm{O(g)}; \quad \bar{D}(\mathrm{N{-}O})$$

enthalpies of pyo (89.6 ± 1.7 kJ $\mathrm{mol^{-1}}$, calculated above), py (140 ± 0.7 kJ $\mathrm{mol^{-1}}$, Table 2), and the oxygen atom (249.17 ± 0.01 kJ $\mathrm{mol^{-1}}$).[18] This value was then used for calculations based on the gas-phase reaction shown below.

$$\mathrm{bipyo(g)} \longrightarrow \mathrm{bipy(g)} + 2\,\mathrm{O(g)}; \quad 2\,\bar{D}(\mathrm{N{-}O})$$

The standard molar enthalpy of formation of crystalline bipy (216.4 ± 7.4 kJ $\mathrm{mol^{-1}}$) was taken from Table 2. The selected enthalpy of sublimation (81.93 ± 0.33 kJ $\mathrm{mol^{-1}}$)[19] was chosen because of its small standard deviation. This leads to a value for the standard molar enthalpy of formation of bipyo, $\Delta H_f^\ominus$(bipyo,g) = 196.6 ± 8.2 kJ $\mathrm{mol^{-1}}$, which leads to an enthalpy of sublimation of 180 ± 10 kJ $\mathrm{mol^{-1}}$. From the $\Delta H_R^\ominus$ values the enthalpies for the reactions given below were derived,

$$\mathrm{MCl_2{\cdot}}n\mathrm{L(c)} \longrightarrow \mathrm{MCl_2(c)} + n\mathrm{L(g)}; \quad \Delta H_D^\ominus$$

$$\mathrm{MCl_2{\cdot}}n\mathrm{L(c)} \longrightarrow \mathrm{MCl_2(g)} + n\mathrm{L(g)}; \quad \Delta H_M^\ominus$$

where $\Delta H_D^\ominus = -\Delta H_R^\ominus + n\Delta H_c^{g\ominus}(\mathrm{L})$ and $\Delta H_M^\ominus = \Delta H_D^\ominus + \Delta H_c^{g\ominus}(\mathrm{MCl_2})$. The last terms in these expressions, the enthalpy of sublimation of ligand (L) and metal halide, respectively, are listed in Table 2. The trends in variation of these parameters are very close to the enthalpy of formation of the adducts. The mean dissociation enthalpy of the metal–oxygen bond can be obtained through the reaction in the gaseous phase for pyo or bipyo (below), where $\bar{D}(\mathrm{M{-}O}) = \Delta H_g^\ominus/n$. The enthalpy $\Delta H_g^\ominus$ is

$$\mathrm{MCl_2{\cdot}}n\mathrm{L(g)} \longrightarrow \mathrm{MCl_2(g)} + n\mathrm{L(g)}; \quad \Delta H_g^\ominus$$

related to $\Delta H_M^\ominus$ by the expression $\Delta H_g^\ominus = \Delta H_M^\ominus - \Delta H_S^\ominus$, where the last value is the enthalpy of sublimation of the adduct (see Table 3). However, to calculate $\bar{D}$(M–O) from $\Delta H_g^\ominus$ values, it was first assumed that $\Delta H_S^\ominus = \Delta H_c^{g\ominus}(\mathrm{L})$,[20] a hypothesis which has been recently tested for some sublimate adducts, giving results that show its validity, to within ±10 kJ $\mathrm{mol^{-1}}$.[21] The standard enthalpy of metal–ligand bond breaking in the gaseous phase, $\Delta H_g^\ominus$, decreases from zinc to mercury (Table 3). As before,[12,22] equivalence of the donor atoms was assumed for each bidentate ligand. Therefore it is possible to compare $\bar{D}$(M–O) of pyo and bipyo. Thus, for a given metal, $\bar{D}$(M–O) is higher for pyo than bipyo, showing that pyo is a better ligand; *e.g.* $HgCl_2$, $\bar{D}$(M–O) values are 44 and 108 kJ $\mathrm{mol^{-1}}$, for bipyo and pyo, respectively.

The mean enthalpies of metal–ligand bonds for all adducts of the zinc group are higher for the mono-adducts, particularly for those of zinc and cadmium with pyo. The same behaviour was observed for pyridine (py), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen) adducts.[12] For these bidentate ligands, the mean metal–ligand bond enthalpies are similar for zinc (116 kJ $\mathrm{mol^{-1}}$ for both ligands) and cadmium (118 and 121 kJ $\mathrm{mol^{-1}}$ for bipy and phen, respectively) adducts, in contrast to the low values for adducts of mercury (60 and 71 kJ $\mathrm{mol^{-1}}$ for bipy and phen, respectively). Adducts of zinc and cadmium with bipyo have $\bar{D}$(M–O) = 115 and 103 kJ $\mathrm{mol^{-1}}$, respectively, with an extremely low value for mercury (44 kJ $\mathrm{mol^{-1}}$; much lower than those found for metal–nitrogen bonds). This result appears to confirm the very much reduced tendency of mercury to bond to oxygen ligand donors.[23]

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