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# Thermochemistry of adducts of tin(IV) chloride with heterocyclic bases

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**Abstract**

The compounds [$SnCl_4(L)_n$] (where L is pyridine (py), 4-methylpyridine (γ-pico), 3-methylpyridine (β-pico), piperidine (pipd), morpholine (morph), piperazine (pipz), 3-cyanopyridine (3-cyanopy), 4-cyanopyridine (4-cyanopy), quinoline (quin) or 2,2′-bipyridine (bipy) and $n = 2, 1$ or 3/2) were synthesized and characterized by elemental analysis, melting points, thermal studies and IR spectroscopy. The enthalpies of dissolution of adducts, tin(IV) chloride and ligands in 1,2-dichloroethane or 25% (v/v) aqueous HCl 1.2 M in methanol were measured and, by using thermochemical cycles, the following thermochemical parameters for the adducts have been determined: the standard enthalpies for the Lewis acid/base reaction ($\Delta_r H^\circ$), the standard enthalpies of formation ($\Delta_f H^\circ$), the standard enthalpies of decomposition ($\Delta_D H^\circ$), the lattice standard enthalpies ($\Delta_M H^\circ$) and the standard enthalpies for the Lewis acid/base reaction in the gaseous phase ($\Delta_r H^\circ$). The mean standard enthalpies of the tin–nitrogen bonds ($\bar{D}_{(Sn-N)}$) have been estimated. Based on these last values, the basicity orders: pipd > morph > γ-pico = β-pico > py > 4-cyanopy > 3-cyanopy and pipz > quin are obtained.

*Keywords:* Sn–N bonds; Tin(IV) chloride; Thermochemical parameters; Heterocyclic bases; Thermochemistry

## 1. Introduction

The acceptor properties of tin(IV) chloride are well established in the literature and the synthesis of numerous adducts have been reported. The main emphasis of the studies made on this kind of compounds has been on searching for a physical approach to the stereochemistry and thermodynamic stability of them [1]. Among the adducts studied, it is found adducts of tin(IV) chloride with ligands containing nitrogen as the donor atom [1–4]. However, little have been done for determining the energies evolved in the adduct formation. There is a lack of thermodynamical data for these compounds. No information about the enthalpies of dissociation of the tin(IV)–nitrogen bonds is available.

In this paper, we described the synthesis of adducts of tin(IV) chloride with heterocyclic amines with the purpose of obtaining the enthalpies involved in the formation of the adducts. Correlations between the bond dissociation enthalpies and other thermochemical parameters are also established. Inductive effects on the energy of the Sn–N bonds due to the substitution of one hydrogen atom of the pyridine ring by the electronic donator methyl group, or by the electronic withdrawing cyano group, as well as, the effect of the substitution of one carbon atom in the piperidine ring by the more electronegative nitrogen or oxygen atoms, were also studied.

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## 2. Experimental

Due to the moisture sensitivity and toxic nature of the compounds, all preparations and manipulations were made under a dry nitrogen atmosphere.

### 2.1. *Chemicals*

Tin(IV) chloride (99%, Aldrich) was purified by the method of Hildebrand and Caster [5]. Pyridine (A.C.S. Reagent), 3-methylpyridine (p.a. Baker), 4-methylpyridine (p.a. Baker), piperidine (99% RPE Analyticals, Carlo Erba), morpholine (99%, A.C.S. Aldrich) and quinoline (98%, Aldrich) were purified by distillation using an efficient column and stored over 4 Å molecular sieves (bp obtained: 111–112, 139–140, 140–141, 103–104, 123–124 and 111–112/120 mm Hg, respectively). Piperazine (99%, Aldrich) was purified by recrystallization from methanol (m.p.: 107–108 °C). 3-Cyanopyridine (98%, Aldrich) and 4-methylpyridine (98%, Aldrich) were purified by recrystallization from methanol (m.p.: 48–50 and 78–80 °C, respectively). 2,2′-Bipyridine (99%, Aldrich) was purified by recrystallization from ethanol according to the method described by Gallagher et al. [6] (m.p.: 193–194 °C). Solvents used in the synthesis and calorimetric measurements were purified by distillation and stored over Linde 4 Å molecular sieves.

### 2.2. *Analytical*

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. Tin was determined by gravimetry as stannic oxide following precipitation of hydrated stannic oxide by ammonia solution from the nitric acid solution of the adducts. The precipitate was ignited to stannic oxide. The filtrate was used for the determination of chloride as silver chloride, using 0.1 M $AgNO_3$ solution.

### 2.3. *Synthesis of the adducts*

The adducts were obtained from the reaction of tin(IV) chloride and ligands in solution. A typical procedure is given bellow.

#### 2.3.1. *$SnCl_4$–py*

On mixing a solution of 1.00 ml (8.55 mmol) of $SnCl_4$ in 10 ml of carbon tetrachloride with 1.40 ml (17.38 mmol) of pyridine, under a dry nitrogen atmosphere current, a white solid appeared. The stirring was kept during several hours. The solid was filtered, washed with three portions of petroleum ether and dried in vacuum and stored in a desiccator over

Table 1
Yields on preparation, melting points, appearance and analytical data of the adducts

| Compound | Yield/% | Melting point[a]/°C | Appearance[b] | C | | H | | N | | Sn | | Cl | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| $[SnCl_4(py)_2]$ | 100 | 338–340[c] | wh. pw. | 28.69 | 28.77 | 2.41 | 2.45 | 6.69 | 6.76 | 28.35 | 28.45 | 33.87 | 33.30 |
| $[SnCl_4(\beta\text{-pico})_2]$ | 97 | 316–318 | wh. pw. | 32.26 | 32.62 | 3.16 | 3.17 | 6.27 | 6.24 | 26.57 | 26.56 | 31.74 | 32.01 |
| $[SnCl_4(\gamma\text{-pico})_2]$ | 100 | 335–337 | wh. pw. | 32.26 | 31.94 | 3.16 | 3.19 | 6.27 | 6.30 | 26.57 | 26.54 | 31.74 | 32.04 |
| $[SnCl_4(\text{pipd})_2]$ | 100 | 216–218 | wh. pw. | 27.88 | 27.60 | 5.15 | 5.28 | 6.50 | 6.48 | 27.55 | 27.65 | 32.92 | 32.99 |
| $[SnCl_4(\text{morph})_2]$ | 100 | 203–205 | wh. pw. | 22.10 | 21.89 | 4.17 | 4.22 | 6.44 | 6.20 | 27.30 | 27.28 | 32.62 | 32.80 |
| $[SnCl_4(\text{pipz})_{3/2}]$ | 100 | 270–272 | wh. pw. | 18.49 | 18.28 | 4.36 | 4.50 | 10.78 | 10.55 | 30.46 | 30.50 | 36.39 | 36.66 |
| $[SnCl_4(3\text{-cyanopy})_2]$ | 92 | 262–264 | wh. pw. | 30.75 | 30.45 | 1.72 | 1.80 | 11.95 | 11.88 | 25.32 | 25.35 | 30.25 | 30.40 |
| $[SnCl_4(4\text{-cyanopy})_2]$ | 92 | 267–268 | wh. pw. | 30.75 | 30.63 | 1.72 | 1.93 | 11.95 | 11.80 | 25.32 | 25.36 | 30.25 | 30.43 |
| $[SnCl_4(\text{quin})_{3/2}]$ | 100 | 225–227 | wh. crs. | 35.70 | 36.04 | 2.33 | 2.55 | 4.63 | 4.74 | 26.13 | 26.05 | 31.22 | 31.01 |
| $[SnCl_4(\text{bipy})]$ | 100 | 360[d] | wh. pw. | 28.83 | 28.89 | 1.94 | 2.10 | 6.72 | 6.88 | 28.48 | 28.49 | 34.03 | 33.81 |

[a] Melting point with decomposition.

[b] wh., white; pw., powder; crs., crystals.

[c] Partial sublimation.

[d] Without melting till 360 °C.

calcium chloride. All the adducts were prepared with a molar ratio tin(IV)/ligand of 1/2.

### 2.4. *Infrared (IR) spectra*

Spectra were obtained with samples in KBr matrix for adducts and solid ligands. For liquid ligands, a film of the ligand sandwiched between NaCl plates was used. A Perkin Elmer 1600 series FTIR spectrophotometer in the 4000–400 $\text{cm}^{-1}$ region was used.

### 2.5. *Thermal studies*

TG/DTG and DSC measurements were obtained in argon atmosphere using a Du Pont 951 TG analyzer with samples varying in mass from 5.07 to 11.02 mg (TG/DTG) and from 4.72 to 4.83 mg (DSC) and a heating rate of 10 $\text{K min}^{-1}$ in the 298–1173 K (TG/DTG) and 298–673 K (DSC) temperature ranges. TG calibration for temperature was made using metallic aluminum as a standard (m.p.: 660.37 °C) and the calibration for mass was carried out automatically. The DSC calibration was made using metallic indium as a standard (m.p.: 165.73 °C, $\Delta_s^l H°$: 28.4 $\text{J g}^{-1}$).

### 2.6. *Calorimetric measurements*

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described elsewhere [7]. The solution calorimetric measurements were performed by dissolving samples from 0.9 to 129.7 mg of the adducts or tin(IV) chloride in 100 ml of methanol or 1,2-dichloroethane and the ligand in this last solution maintaining a molar relation equal to the stoichiometry of the adduct. The accuracy of the calorimeter was carried out by determining the heat of dissolution of tris [(hydroxymethyl)amino]methane in 0.1 $\text{mol dm}^{-3}$ HCl. The result ($-29.78 \pm 0.03\ \text{kJ mol}^{-1}$) is in agreement with the value recommended by IUPAC [8] ($-29.763 \pm 0.000\ \text{kJ mol}^{-1}$).

## 3. Results and discussion

All the adducts obtained were solids. For the adduct of pyridine, it was observed when the capillary melting point was determined, its partial sublimation with the decomposition of the residue. For the other

Table 2
Main IR absorption bands ($\text{cm}^{-1}$)[a] of complexes and free ligands

| Compound | $\nu$(N–H) | $\nu$(C–C) | $\nu$(C–N) | Ring | $\nu$(C–O–C) | $\delta$(H–N–C) | $\alpha$(C–C–C) | $\phi$(C–C) | New bands |
|---|---|---|---|---|---|---|---|---|---|
| py | | 1573sh | | | | | 584s | 431m | |
| $[SnCl_4(py)_2]$ | | 1609s | | | | | n.o. | 433m | 1249w |
| γ-pico | | 1585s, 1545s | | 1206s | | | n.o. | 439w | |
| $[SnCl_4(\gamma\text{-pico})_2]$ | | 1627s | | 1214s | | | 557m | n.o. | 1234w |
| β-pico | | 1572sh, 1558s | | 1206m | | | 652sh | n.o. | |
| $[SnCl_4(\beta\text{-pico})_2]$ | | 1579m | | 1188s | | | 659m | | |
| pipd | 3276m | 1467s | | | | 860s, 825m | | | |
| $[SnCl_4(pipd)_2]$ | 3178s | 1455s | | | | 871s, 855m | | | |
| morph | 3320m | 1452s | | | 1097s | 889m, 835s | | | |
| $[SnCl_4(morph)_2]$ | 3120m | 1450s | | | 1114s | 899m, 872s | | | |
| pipz | 3275s | 1461s | | | | 861m, 815s | | | |
| $[SnCl_4(pipz)_{3/2}]$ | 3244s | 1440s | | | | 868m | | | |
| 3-cyanopy | | | 2231s | 1219s | | | | | |
| $[SnCl_4(3\text{-cyanopy})_2]$ | | | 2247m | 1195s | | | | | |
| 4-cyanopy | | | 2236s | 1216s | | | | | |
| $[SnCl_4(4\text{-cyanopy})_2]$ | | | 2243m | 1224m | | | | | |
| quin | | 1596s | | 1031m | | | | n.o. | |
| $[SnCl_4(quin)_{3/2}]$ | | 1596m | | 952m | | | | 1228m | |
| bipy | | 1579s | | 994m | | | | 759vs | |
| $[SnCl_4(bipy)]$ | | 1599s | | 1031m | | | | n.o. | 1320m, 724s |

[a] $\alpha$, ring deformation in plane; $\phi$, ring deformation out of plane; $\nu$, stretching; $\delta$, angular deformation; ring, ring breathing; n.o., not observed. Intensity of bands: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

adducts, the determination of their capillary melting points leaded to the decomposition of the adducts. The yields ranged from 92 to 100 %. The yields, melting points, colors, appearance and analytical data are summarized in Table 1.

### 3.1. *IR spectra*

The more important IR bands are reported in Table 2. Considerable shifts to lower frequencies of the $\nu_{(\mathrm{N–H})}$ bands of the ligands pipd, morph and pipz after coordination are observed. This is indicative of coordination of them through the nitrogen atom of their NH group [9,10]. In the morpholine adduct, the positive shift of the band attributed to the C–O–C stretching vibration, with respect to free morpholine, excludes the possibility of oxygen-to-tin(IV) coordination [9]. The change observed in the H–N–C deformation region (889-815 $\mathrm{cm^{-1}}$) also affords evidence of coordination of the nitrogen atom of the ligands [11]. The coordinated pyridine is distinguished from free pyridine by the presence in the adducts of a weak band at 1250 $\mathrm{cm^{-1}}$ and by the splitting of bands at 584 and 431 $\mathrm{cm^{-1}}$ in free pyridine, to higher frequencies [12]. The IR spectra of β- and γ-picoline adducts show appreciable splitting towards higher frequencies of the bands at 1585–1545 and 1206 $\mathrm{cm^{-1}}$ in the free ligands [13,14]. For 3- and 4-cyanopyridine adducts, this last band is observed at 1195 and 1224 $\mathrm{cm^{-1}}$, respectively (1219 and 1216 $\mathrm{cm^{-1}}$ in free ligands). As the band attributed to the stretching of the nitrile group in the free ligands (2236–2231 $\mathrm{cm^{-1}}$) increases its frequency very little and its intensity decreases after coordination, these exclude the coordination of the ligands trough the nitrogen atom of the nitrile group [15].

Table 3
Thermochemical data of the compounds

| Compound | % Mass lost | | TG temperature range/K | Species lost | DSC peak temperature/K | $\Delta H^\circ$/kJ $\mathrm{mol^{-1}}$ |
|---|---|---|---|---|---|---|
| | Calcd. | Obs. | | | | |
| $[\mathrm{SnCl_4(py)_2}]$ | 100 | 100 | 495–555 | $-2\mathrm{py–SnCl_4}$ | n.o.[a] | |
| $[\mathrm{SnCl_4}(\beta\text{-pico})_2]$ | 100 | 98.6 | 504–548 | Pyrolysis | 388 | 1.74 |
| | | 1.4[b] | | | | |
| $[\mathrm{SnCl_4}(\gamma\text{-pico})_2]$ | 100 | 98.1 | 502–541 | Pyrolysis | n.o. | |
| | | 1.9[b] | | | | |
| $[\mathrm{SnCl_4(pipd)_2}]$ | 11.9 | 11.6[c] | 422–464 | −0.6pipd | 374 | 0.12 |
| | 88.1 | 77.3[c] | 464–681 | $-1.4\mathrm{pipd–SnCl_4}$ | 428 | 0.34 |
| | | 3.7[b] | | | 453 | 2.46 |
| $[\mathrm{SnCl_4(morph)_2}]$ | 100 | 80.3[c] | 500–619 | Pyrolysis | 451 | 2.00 |
| | | 6.9 | 872–937 | | 471 | 1.36 |
| | | 12.8[b] | | | | |
| $[\mathrm{SnCl_4(pipz)_{3/2}}]$ | 100 | 98.6 | 458–494 | Pyrolysis | 386 | 31.35 |
| | | 1.4[b] | | | | |
| $[\mathrm{SnCl_4(3\text{-}cyanopy)_2}]$ | 4.4 | 4.4 | 324–346 | $-0.2\mathrm{SnCl_4}$ | 317 | 0.32 |
| | 95.6 | 88.2[d] | 489–676 | Pyrolysis | 344 | 2.98 |
| | | 9.2[b] | | | | |
| $[\mathrm{SnCl_4(4\text{-}cyanopy)_2}]$ | 100 | 97.9 | 452–491 | Pyrolysis | 545 | 128.38 |
| | | 2.1[b] | | | | |
| $[\mathrm{SnCl_4(quin)_{3/2}}]$ | 100 | 97.5[d] | 379–507 | Pyrolysis | 345 | 5.45 |
| | | 2.5[b] | | | 402 | 8.94 |
| | | | | | 504 | 0.81 |
| $[\mathrm{SnCl_4(bipy)}]$ | 100 | 95.4 | 597–642 | Pyrolysis | n.o. | |
| | | 4.6[b] | | | | |

[a] Not observed.
[b] Residue at 1173 K.
[c] Two overlapping steps.
[d] Three overlapping steps.

Then, the IR data for these adducts, can be interpreted in terms of coordination through the heterocyclic nitrogen atom of the ligands to the tin(IV) atom [12–15]. The IR spectra of the bipyridine adduct shows the appearance of new bands after coordination. Two new bands appear at 1320 and 724 $cm^{-1}$, both of which are absent in free bipy and are due to the adduct formation [16]. The IR spectra of the quin adduct shows the splitting of several bands with respect to the free ligand [17]. A new band is observed at 1228 $cm^{-1}$ after coordination. The IR data of the bipy and quin adducts can be interpreted in terms of coordination of these ligands through the nitrogen atom to the tin(IV) atom [16,17].

### 3.2. *Thermal studies*

Thermogravimetry and derivative thermogravimetry of the adducts show that the thermal dissociation process of the adducts are of different types:

I. $[SnCl_4(L)_2] \rightarrow SnCl_4 + 2L$
II. $[SnCl_4(L)_2] \rightarrow$ pyrolysis
III. $[SnCl_4(L)_2] \rightarrow [SnCl_4(L)_{1.4}] + 0.6L$
$[SnCl_4(L)_{1.4}] \rightarrow$ pyrolysis
IV. $[SnCl_4(L)_2] \rightarrow [(SnCl_4)_{0.8}(L)_2] + 0.2SnCl_4$
$[(SnCl_4)_{0.8}(L)_2] \rightarrow$ pyrolysis

The adduct of py followed process I. Those of β-pico, γ-pico, morph, pipz, 4-cyanopy, quin and bipy followed process II. The adduct of pipd followed process III and the adduct of 3-cyanopy followed process IV.

The DSC curves of the adducts are consistent with TG/DTG data. They present several endothermic peaks due to pyrolysis, partial elimination of ligand or tin(IV) chloride or partial elimination of both ligand and tin(IV) chloride. Table 3 lists the thermoanalytical data of the adducts.

### 3.3. *Calorimetric measurements*

The standard enthalpies of dissolution of tin(IV) chloride, ligands and adducts were obtained as previously reported [7]. Table 4 gives the values obtained for the enthalpies of dissolution of $SnCl_4$ ($\Delta_1 H^\circ$), ligand into the solution of $SnCl_4$ ($\Delta_2 H^\circ$) and of the adduct ($\Delta_3 H^\circ$). Uncertainty intervals given in this table are twice the standard deviation of the means of 3–6 replicate measurements on each compound. Combined errors were calculated from the square root of

Table 4
Enthalpies of dissolution at 298.15 K[a]

| Compound | Calorimetric solvent | Number of experiments | $\Delta_i H^\circ$/kJ $mol^{-1}$ |
|---|---|---|---|
| $SnCl_{4(l)}$ | A | 11 | $(i = 1)$ −137.69 ± 2.09 |
| $py_{(l)}$ | 2:1 $SnCl_4$–A | 5 | $(i = 2)$ −34.82 ± 1.15 |
| $[SnCl_4(py)_2]_{(s)}$ | A | 4 | $(i = 3)$ 14.58 ± 0.21 |
| γ-$pico_{(l)}$ | 2:1 $SnCl_4$–A | 6 | $(i = 2)$ −35.88 ± 0.53 |
| $[SnCl_4(\gamma\text{-pico})_2]_{(s)}$ | A | 5 | $(i = 3)$ 16.27 ± 1.11 |
| $quin_{(l)}$ | 1.5:1 $SnCl_4$–A | 5 | $(i = 2)$ −36.27 ± 0.79 |
| $[SnCl_4(quin)_{3/2}]_{(s)}$ | A | 3 | $(i = 3)$ 24.82 ± 2.03 |
| $SnCl_{4(l)}$ | B | 6 | $(i = 1)$ −78.26 ± 2.28 |
| β-$pico_{(l)}$ | 2:1 $SnCl_4$–B | 4 | $(i = 2)$ −65.20 ± 1.86 |
| $[SnCl_4(\beta\text{-pico})_2]_{(s)}$ | B | 4 | $(i = 3)$ 46.09 ± 1.67 |
| $pipd_{(l)}$ | 2:1 $SnCl_4$–B | 5 | $(i = 2)$ −205.10 ± 2.30 |
| $[SnCl_4(pipd)_2]_{(s)}$ | B | 3 | $(i = 3)$ 22.63 ± 0.62 |
| $morph_{(l)}$ | 2:1 $SnCl_4$–B | 6 | $(i = 2)$ −142.12 ± 3.21 |
| $[SnCl_4(morph)_2]_{(s)}$ | B | 3 | $(i = 3)$ 27.00 ± 1.47 |
| $SnCl_{4(l)}$ | C | 11 | $(i = 1)$ −121.07 ± 0.78 |
| $pipz_{(s)}$ | 1.5:1 $SnCl_4$–C | 3 | $(i = 2)$ −60.63 ± 1.83 |
| $[SnCl_4(pipz)_{1.5}]_{(s)}$ | C | 3 | $(i = 3)$ 36.96 ± 1.15 |
| 3-$cyanopy_{(s)}$ | 2:1 $SnCl_4$–C | 5 | $(i = 2)$ 41.23 ± 2.20 |
| $[SnCl_4(3\text{-cyanopy})_2]_{(s)}$ | C | 3 | $(i = 3)$ 24.56 ± 0.66 |
| 4-$cyanopy_{(s)}$ | 2:1 $SnCl_4$–C | 4 | $(i = 2)$ 50.94 ± 0.96 |
| $[SnCl_4(4\text{-cyanopy})_2]_{(s)}$ | C | 5 | $(i = 3)$ 58.06 ± 2.91 |

[a] A: 1–2% water in 1,2-dichloroethane; B: dry 1,2-dichloroethane; C: methanol.

Table 5

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

| Compound | $\Delta_r H^\circ$ | $\Delta_f H^\circ$ | $\Delta_l^g H^\circ$ or $\Delta_s^g H^\circ$ | $\Delta_M H^\circ$ | $\Delta_D H^\circ$ | $\Delta_r H^\circ$(g) | $\bar{D}_{(\mathrm{Sn-N})}$ |
|---|---|---|---|---|---|---|---|
| SnCl$_{4(l)}$ | | 511.3[a] | 39.8[a] | | | | |
| py$_{(l)}$ | | 101.2 ± 0.7[b] | 40.2 ± 0.0[b] | | | | |
| γ-pico$_{(l)}$ | | 58.5 ± 1.1[b] | 45.3 ± 0.4[b] | | | | |
| β-pico$_{(l)}$ | | 61.9 ± 0.5[b] | 44.4 ± 0.0[b] | | | | |
| pipd$_{(l)}$ | | 88.0[b] | 39.1 ± 1.8[b] | | | | |
| morph$_{(l)}$ | | −170.2[c] | 42.3[c] | | | | |
| pipz$_{(s)}$ | | −45.6 ± 1.6[b] | 84.2[c] | | | | |
| 3-cyanopy$_{(s)}$ | | 38.0 ± 3.2[d] | 89.0 ± 2.8[d] | | | | |
| 4-cyanopy$_{(s)}$ | | 40.9 ± 3.9[d] | 83.6 ± 3.5[d] | | | | |
| quin$_{(l)}$ | | 116.1 ± 1.9[d] | 59.7[d] | | | | |
| [SnCl$_4$(py)$_2$]$_{(s)}$ | −187.09 ± 2.40 | −496.0 ± 2.9 | | −307.3 ± 3.1 | 267.5 ± 2.4 | −267.1 ± 3.1 | 133.6 ± 1.6 |
| [SnCl$_4$(γ-pico)$_2$]$_{(s)}$ | −189.54 ± 2.43 | −583.8 ± 3.4 | | −319.9 ± 3.3 | 280.1 ± 2.6 | −274.6 ± 3.3 | 137.3 ± 1.7 |
| [SnCl$_4$(β-pico)$_2$]$_{(s)}$ | −190.35 ± 3.38 | −577.9 ± 3.6 | | −706.5 ± 4.1 | 279.2 ± 3.4 | −274.6 ± 3.9 | 137.3 ± 2.0 |
| [SnCl$_4$(pipd)$_2$]$_{(s)}$ | −305.99 ± 3.30 | −993.3 ± 3.4 | | −424.0 ± 5.3 | 384.2 ± 4.9 | −384.9 ± 5.6 | 197.5 ± 2.8 |
| [SnCl$_4$(morph)$_2$]$_{(s)}$ | −247.38 ± 4.20 | −1099.1 ± 4.7 | | −371.8 ± 5.0 | 332.0 ± 3.1 | −329.5 ± 5.2 | 164.8 ± 2.6 |
| [SnCl$_4$(pipz)$_{3/2}$]$_{(s)}$ | −218.96 ± 2.30 | −798.7 ± 3.5 | | −385.1 ± 3.8 | 345.3 ± 2.7 | −300.9 ± 3.5 | 200.6 ± 2.3 |
| [SnCl$_4$(3-cyanopy)$_2$]$_{(s)}$ | −104.40 ± 2.40 | −539.7 ± 8.1 | | −322.1 ± 6.4 | 283.32 ± 6.14 | −233.2 ± 7.0 | 116.6 ± 3.5 |
| [SnCl$_4$(4-cyanopy)$_2$]$_{(s)}$ | −128.19 ± 3.14 | −557.7 ± 8.5 | | −335.2 ± 8.1 | 295.4 ± 7.7 | −251.6 ± 8.7 | 125.8 ± 4.4 |
| [SnCl$_4$(quin)$_{3/2}$]$_{(s)}$ | −198.78 ± 3.02 | −535.9 ± 4.3 | | −328.1 ± 4.3 | 288.3 ± 3.4 | −268.4 ± 4.0 | 178.9 ± 2.7 |

[a] Ref. [19].

[b] Ref. [20].

[c] Ref. [21].

[d] Ref. [22].

the sum of the squares of the component errors. The adduct of bipyrine is extremely insolved in most solvents and it was not possibly determined its enthalpy of dissolution.

From the values obtained for the standard enthalpies of dissolution and by using appropriate thermochemical cycles [7,18], the following thermochemical parameters were determined: the standard enthalpies of the acid/base reactions ($\Delta_r H^\circ$), the standard enthalpies of formation ($\Delta_f H^\circ$), the standard enthalpies of decomposition ($\Delta_D H^\circ$), the standard lattice enthalpies ($\Delta_M H^\circ$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\circ(g)$). The $\Delta_r H^\circ(g)$ values can be used to calculate the standard enthalpies of the Sn–N bonds [18], being equal to $\bar{D}_{(\mathrm{Sn–N})} = \Delta_r H^\circ(g)/n$ (where $n = 2$ or 3/2). Table 5 lists the values obtained for all these thermochemical parameters for the adducts. For the determination of $\Delta_r H^\circ(g)$, it was necessary to assume that the molar standard enthalpies of sublimation of the adducts were equal to the enthalpies of sublimation or vaporization of 1 mol of the respective ligand [23,24], as melting points and thermal studies showed that the adducts decomposed on heating and were not found in the liquid phase and probably, not in the gaseous phase.

Based on the $\Delta_r H^\circ$ values for the adducts, we obtain the basicity order: pipd > morph > β-pico > γ-pico > py > 4-cyanopy > 3-cyanopy and pipz > quin. Using the $\bar{D}_{(\mathrm{Sn–N})}$ values, we obtain the basicity order: pipd > morph > γ-pico = β-pico > py > 4-cyanopy > 3-cyanopy and pipz > quin. The expected order for pyridine and derivatives would be γ-pico > $\beta$-pico > py > 3-cyanopy > 4-cyanopy due to an inductive effect of substitution of one hydrogen atom in the pyridine ring, by the electron donator methyl group in β- or γ-pico or by the electron withdrawing cyano group in 3- or 4-cyanopy. This causes the increase or the decrease, respectively, of the electronic density available for bonding on the nitrogen atom of the ring, relative to unsubstituted pyridine. The effect is stronger in *p*-substitution than in *m*-substitution. The inversion observed between 4- and 3-cyanopy could be due to the contribution of another kind of interaction like hydrogen bonding between the nitrogen atom of the cyano groups and the carbon atoms from pyridine rings [22], being this effect stronger for 4- than for 3-cyanopyrine. Otherwise, the basicity order observed is the expected order.

The expected basicity order for saturated heterocyclic amines would be pipd > morph due to an inductive effect of substitution of one carbon atom in the ring of pipd by the more electronegative atom of oxygen, leading to the decrease of the electronic density available for bonding on the nitrogen atom of the ring. The order observed matches the expected order.

As a whole it is observed that the mean tin–nitrogen coordinate bond dissociation energies for the adducts here studied, are higher than the mean dissociation energies of the tin(IV)–oxygen or tin(IV)–sulfur bonds in comparable adducts of tin(IV) chloride with amides or thioamides [25,26].

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