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# Thermochemistry of adducts of zinc(II) dialkyldithiocarbamate with 2,2′-bipyridine

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## Abstract

The enthalpies of dissolution of adducts, Zn(II) dialkyldithiocarbamate and bipy, $Zn(S_2CNR_2)_2 \cdot C_{10}H_8N_2$, ($R{=}C_2H_5$, $n$-$C_3H_7$, $n$-$C_4H_9$, i-$C_4H_9$ and $n$-$C_5H_{11}$), in acetone were measured and the following thermochemical parameters for the adducts determined: the standard enthalpies for the Lewis acid/base reaction ($\Delta_r H^0$), the standard enthalpies of formation ($\Delta_f H^0$), the standard enthalpies of decomposition ($\Delta_D H^0$), the lattice standard enthalpies ($\Delta_M H^0$) and the standard enthalpies of the Lewis acid/base reactions in the gas phase ($\Delta_r H^0(g)$). The mean standard enthalpies of the zinc–nitrogen bonds have been estimated and range from 54 to 138 kJ mol$^{-1}$. The standard enthalpies of sublimation of the adducts were determined by differential scanning calorimetry and estimation methods. The thermodynamics of adduct formation between Zn(II) dialkyldithiocarbamate and bipyridine in acetone solution was determined by calorimetric titration. The results indicate the following order of the enthalpy changes for the interaction: $Et<Pr^n<Pe^n<Bu^n<Bu^i$. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Zinc; Dialkyldithiocarbamate; Enthalpy; Calorimetry; Zn–N bonds

## 1. Introduction

The pronounced ability of dithiocarbamate ligands to chelate metals has received much attention [1]. This property has been used for determination of a wide range of metals and in various other applications. Interest in the chemistry of dithiocarbamates lies not only in analytical, but also in their industrial applications [2].

Investigation in this field was initially directed to the structural features of the complexes [1] and their wide analytical applicability [3]. However, thermochemical interest in these complexes has progressively increased. An important review of the thermochemistry of dithiocarbamate complexes, including dithiocarbamates and dithiophosphates, also included thermal decomposition, reaction-solution calorimetry and metal–sulfur bond dissociation enthalpy [4,5], and has been followed by more recent works [6–8].

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The aim of the present paper is to synthesize and characterize the adducts of zinc(II) dialkyldithiocarbamate with 2,2′-bipyridine, i.e. $Zn(S_2CNR_2)_2{\cdot}C_{10}H_8N_2$, (where $R{=}C_2H_5$, $n$-$C_3H_7$, $n$-$C_4H_9$, i-$C_4H_9$ and $n$-$C_5H_{11}$), and to determine the enthalpies involved in the formation of the adducts by reaction-solution and titration calorimetry in order to understand the effect of the length of the alkyl chain attached to the nitrogen of the dithiocarbamate ligand.

## 2. Experimental

Due to the moisture sensitivity of the compounds, all the manipulations and preparations were carried out in a dry nitrogen atmosphere or under reduced pressure.

### 2.1. Chemicals

The solvents used in all preparations were purified by distillation and stored over Linde 4 Å molecular sieves. Diethyl, di-*n*-propyl, di-*n*-butyl, di-iso-butyl and di-*n*-pentylamine (Merck) as well as carbon disulfide (Merck), were purified by distillation. Zinc(II) chloride (Vetec) was purified by recrystallisation from ethanol and dehydrated under reduced pressure at 433 K for 18 h. 2,2′-Bipyridine (Aldrich) was purified by recrystallisation from ethanol according to the method described by Gallagher et al. [9]. Dried acetone was chosen as the calorimetric solvent due to the good thermal effect produced and by its ability to dissolve the chelates, adducts and 2,2′-bipyridine.

### 2.2. Synthesis

$R_2NH_2Cl$ and $R_2NH_2S_2CNR_2$ were prepared according to literature methods [10,11].

Zn(II) dialkyldithiocarbamate was prepared by the reaction of $ZnCl_2$ and $R_2NH_2S_2CNR_2$ (molar ratio 1:2) with stirring in an ice-salt bath, using acetone as solvent and dry nitrogen atmosphere [12]. The white solid formed was filtered, washed with several portions of ether and dried for 8 h in vacuum.The adducts were synthesized by adding an acetone solution of bipyridine to a solution of Zn(II) dialkyldithiocarbamate (molar ratio 2:1) in acetone, with stirring and heating. The mixture was cooled for 12 h and the yellow solid formed was filtered, washed with several portions of ether and dried for several hours in vacuum. The yield ranged from 69 to 78%. Microanalysis for carbon, hydrogen and nitrogen were obtained with a Perkin-Elmer Elemental Analyser, model PE-2400. Zinc was determined with a GBC Atomic Absortion Spectrophotometer, model 908-AA.

### 2.3. Physical measurements

The melting points of all compounds were determined by means of a MICROQUÍMICA model MQAPF-301 apparatus. Infra-red spectra were obtained from KBr pellets, in the region 4000–200 $cm^{-1}$ using a BOMEM, model MB-102 series FTIR spectrophotometer.

### 2.4. Thermal measurements

TG curves were obtained with a Shimadzu model TGA-50 thermobalance at a heating rate of 10°C $min^{-1}$ and a nitrogen atmosphere. The carrier gas flow was maintained at 3.33 $cm^3\ s^{-1}$. The sample mass was $5.0\pm0.5$ mg.

DSC curves were obtained with a differential scanning calorimeter, Shimadzu model DSC-50, at a heating rate of 10 K $min^{-1}$ in nitrogen atmosphere. The carrier gas flow was maintained at 3.33 $cm^3\ s^{-1}$. The sample mass was $5.0\pm0.5$ mg.

### 2.5. Calorimetric measurements

All the solution calorimetric determinations were made with an LKB 8700-1 precision calorimeter as described previously [13]. The solution calorimetric measurements were performed by dissolving samples of 15.40–72.53 mg of the adducts or bipyridine in 100 ml of acetone and the Zn(II) chelate in a solution of bipyridine in acetone, maintaining a molar ratio equal to 1:1. The accuracy of the calorimeter was checked by determining the heat of dissolution of tris(hydroxy methyl)amino methane in 0.1 mol $dm^{-3}$ HCl. The value obtained ($29.78\pm0.03$ kJ $mol^{-1}$) is in agreement with the value recommended by IUPAC [14] ($-29.76\pm0.03$ kJ $mol^{-1}$). The titration calorimetric measurements were performed in acetone as solvent. A solution of 2 ml of bipyridine (0.6257 M) in

Table 1
Yields (%), melting points (°C), appearance and analytical data on the adducts

| Compound | Melting point (°C) | Appearance | C | | H | | N | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calculated | Found | Calculated | Found | Calculated | Found | Calculated | Found |
| $Zn(S_2CNEt_2)_2 \cdot bipy$ | 185–187 | White crystals | 46.37 | 46.56 | 5.45 | 5.53 | 10.81 | 10.70 | 12.62 | 12.02 |
| $Zn(S_2CNPr^n_2)_2 \cdot bipy$ | 158–161 | White crystals | 50.20 | 49.98 | 6.32 | 5.92 | 9.76 | 9.72 | 11.38 | 11.21 |
| $Zn(S_2CNBu^n_2)_2 \cdot bipy$ | 136–137 | White crystals | 53.36 | 53.45 | 7.04 | 6.89 | 8.89 | 9.12 | 10.37 | 10.29 |
| $Zn(S_2CNBu^i_2)_2 \cdot bipy$ | 175–178 | White crystals | 53.36 | 53.20 | 7.04 | 6.88 | 8.89 | 8.86 | 10.37 | 10.22 |
| $Zn(S_2CNPe^n_2)_2 \cdot bipy$ | 93–94 | White crystals | 55.99 | 55.93 | 7.64 | 7.48 | 8.16 | 8.46 | 9.52 | 9.47 |

acetone at 298.15±0.05 K was incrementally added in 0.1 ml portions with a Hart Scientific 4285 syringe to 25 ml of a solution of 0.01 M Zn(II) dialkyldithiocarbamate in acetone in the calorimetric vessel. The calorimeter performance and details of operation were previously described [13]. Dilutions of the solutions of Zn(II) dialkyldithiocarbamate and 2,2′-bipyridine were performed to correct for dilution effects.

## 3. Results

All the adducts obtained were solids. The yields, melting points, colours, appearance and analytical data are summarized in Table 1.

The more important IR bands are reported in Table 2. The assignments for Zn(II) chelates are based on those of Bell et al. [15]. The $\nu_{C=C}$, $\nu_{C=S}$ and $\nu_{N-C-S}$ shift to lower frequencies in the adducts relative to those of the uncoordinated Zn(II) chelate, indicating that bipyridine is coordinated to zinc. These shifts are more marked than those observed for the formation of Zn(II) dialkyldithiocarbamate [10,16–18]. The infrared spectra of bipy adducts also show the appearance of a new band in the region 1023–1015 cm$^{-1}$ that is absent in free bipy, and is due to adduct formation [19].

The TG–DTG curves of the adducts, Fig. 1, show that the thermal dissociation process of the adducts is

$$[Zn(S_2CNR_2)_2 \cdot bipy] \rightarrow Zn(S_2CNR_2)_2 + bipy$$

$$Zn(S_2CNR_2)_2 \rightarrow pyrolysis$$

The DSC curves of the adducts are consistent with the TG–DTG data and show two endothermic peaks: the first is due to melting of adducts and the second is due to pyrolysis of Zn(II) dialkyldithiocarbamate. Table 3 lists the thermochemical data for the adducts.

The standard enthalpies of dissolution of bipy, Zn(II) dialkyldithiocarbamate and adducts were obtained as previously reported [6,7,12]. Table 4 gives the values obtained for the enthalpies of dissolution of bipy ($\Delta_1 H^\theta$), those of Zn(II) dialkyldithiocarbamate into the solution of bipy (molar ratio 1:1) ($\Delta_2 H^\theta$) and those of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in the table are twice the standard deviation of the means of four replicate measurements. Combined errors were calculated from the square root of the sum of the square of the component errors. The standard enthalpy of reaction ($\Delta_r H^\theta$) for

Table 2
Infra-red data for bipy and its adducts (cm$^{-1}$)[a]

| Compound | $\nu_{C=C}$ | $\nu_{C=N}$ | $\nu_{N-C-S}$ | Ligand bands | |
|---|---|---|---|---|---|
| Bipy | | | | 1579 s | |
| $Zn(S_2CNEt_2)_2 \cdot bipy$ | 1560 m, 1542 w | 1475 s | 1154 w, 993 s | 1593 m | 1017 s |
| $Zn(S_2CNPr^n_2)_2 \cdot bipy$ | 1561 m, 1542 w | 1475 s | 1146 s, 981 s | 1596 m | 1016 s |
| $Zn(S_2CNBu^n_2)_2 \cdot bipy$ | 1542 w | 1474 s | 1140 m, 990 m | 1593 m | 1017 s |
| $Zn(S_2CNBu^i_2)_2 \cdot bipy$ | 1560 m, 1542 w | 1473 s | 1150 m, 992 m | 1596 m | 1023 s |
| $Zn(S_2CNPe^n_2)_2 \cdot bipy$ | 1560 w | 1461 w | 1069 w | 1599 m | 1015 s |

[a] $\nu$: Stretching; intensity of bands — s: strong; m: medium; w: weak.

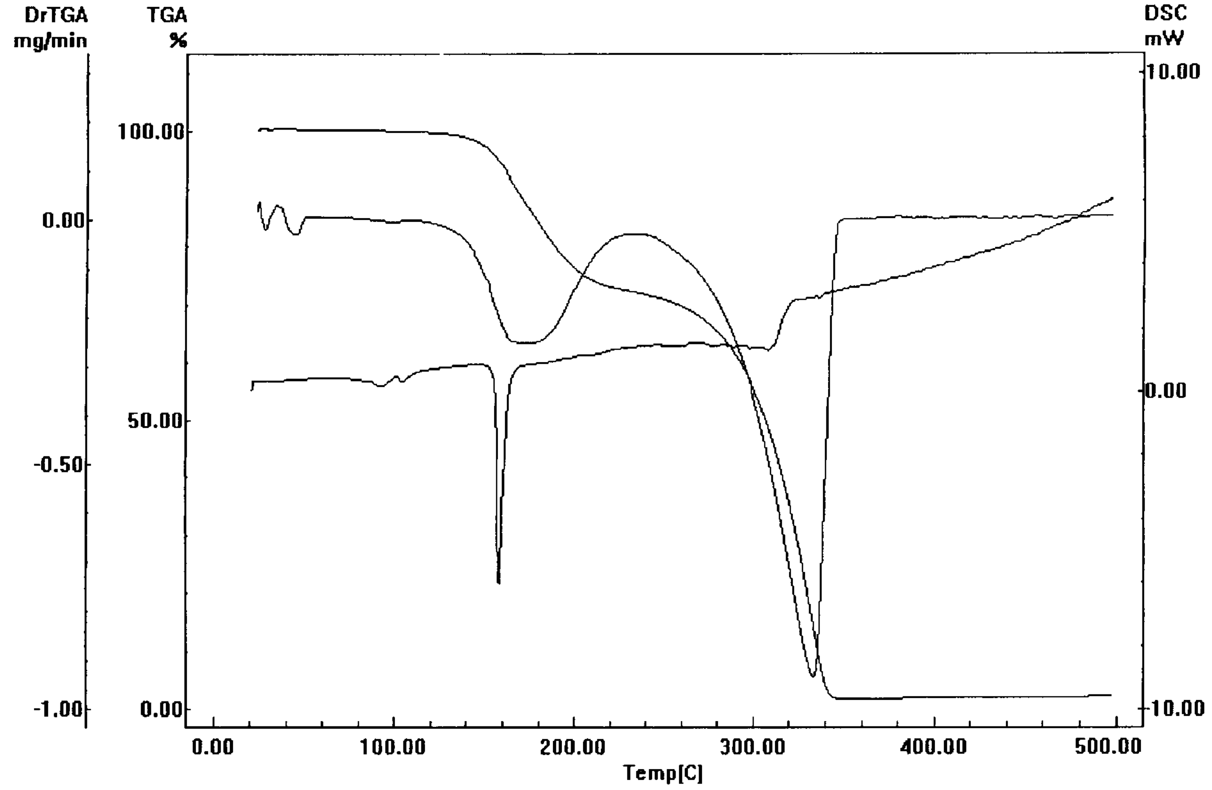

Fig. 1. Superimposed TG/DTG/DSC curves of $Zn(S_2CNPr^n_2)_2\cdot bipy$.

Table 3
Thermoanalytical data on the adducts

| Compound | Mass loss (%) | | TG/temperature range (K) | Species lost | DSC peak temperature (K) | Enthalpy (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| | Calculated | Observed | | | | |
| $[Zn(S_2CNEt_2)_2\cdot bipy]$ | 30.15 | 31.91 | 397–511 | –Bipy | 454 | 51.60$^{a}$ |
| | 69.85 | 66.29 | 511–613 | $-Zn(S_2CNEt_2)_2$$^{b}$ | 536 | 52.80 |
| | | | | | | 1.81$^{c}$ |
| $[Zn(S_2CNPr^n_2)_2\cdot bipy]$ | 27.20 | 27.81 | 392–508 | –Bipy | 424 | 49.50 |
| | 72.80 | 70.17 | 508–623 | $-Zn(S_2CNPr^n_2)_2$ | 594 | 69.30 |
| | | | | | | 1.99$^{c}$ |
| $[Zn(S_2CNBu^n_2)_2\cdot bipy]$ | 24.78 | 24.56 | 392–498 | –Bipy | 452 | 50.60 |
| | 75.22 | 72.26 | 498–634 | $-Zn(S_2CNBu^n_2)_2$ | 562 | 60.20$^{a}$ |
| | | | | | | 3.17$^{c}$ |
| $[Zn(S_2CNBu^i_2)_2\cdot bipy]$ | 24.78 | 26.15 | 412–507 | –Bipy | 452 | 81.5 |
| | 75.22 | 72.64 | 507–617 | $-Zn(S_2CNBu^i_2)_2$ | 562 | 43.10 |
| | | | | | | 1.21$^{c}$ |
| $[Zn(S_2CNPe^n_2)_2\cdot bipy]$ | 22.29 | 21.03 | 377–503 | –Bipy | 364 | 34.9 |
| | 77.71 | 63.51 | 503–673 | $-Zn(S_2CNPe^n_2)_2$ | 629 | 102.00 |
| | | | | | | 6.09$^{c}$ |

[a] Duble peak.

[b] Prolysis of the compound formed.

[c] Ridue at 773 K.

Table 4
Enthalpies of dissolution at 298.15 K

| Compound | Calorimetric solvent | Solution | No. of experiments | $\Delta_i H^\theta$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| Bipy | Acetone | $A_1$ | 6 | 18.66±0.02 |
| $Zn(S_2CNEt_2)_2$[a] | $A_1$ | $A_2$ | 6 | 13.35±0.49 |
| $Zn(S_2CNEt_2)_2$·bipy | Acetone | $A_3$ | 6 | 58.20±0.02 |
| Bipy | Acetone | $B_1$ | 6 | 18.66±0.02 |
| $Zn(S_2CNPr^n_2)_2$[a] | $B_1$ | $B_2$ | 6 | 39.99±0.01 |
| $Zn(S_2CNPr^n_2)_2$·bipy | Acetone | $B_3$ | 6 | 93.25±0.05 |
| Bipy | Acetone | $C_1$ | 6 | 18.66±0.02 |
| $Zn(S_2CNBu^n_2)_2$[a] | $C_1$ | $C_2$ | 6 | 27.74±0.01 |
| $Zn(S_2CNBu^n_2)_2$·bipy | Acetone | $C_3$ | 6 | 71.33±0.06 |
| Bipy | Acetone | $D_1$ | 6 | 18.66±0.02 |
| $Zn(S_2CNBu^i_2)_2$[a] | $D_1$ | $D_2$ | 6 | 36.83±0.05 |
| $Zn(S_2CNBu^i_2)_2$·bipy | Acetone | $D_3$ | 6 | 78.95±0.04 |
| Bipy | Acetone | $E_1$ | 6 | 18.66±0.02 |
| $Zn(S_2CNPe^n_2)_2$[a] | $E_1$ | $E_2$ | 6 | 35.53±0.01 |
| $Zn(S_2CNPe^n_2)_2$·bipy | Acetone | $E_3$ | 6 | 69.93±0.03 |

[a] Always in a molar relation donor/acceptor of 1/1.

reaction (1)

$$\mathrm{Zn(S_2CNR_2)_2(cr) + bipy(cr)} \rightarrow \mathrm{Zn(S_2CNR_2)_2 \cdot bipy(cr)}; \quad \Delta_r H^\theta \qquad (1)$$

was obtained from the standard enthalpy changes of reactions 2–5 in solution

$$\mathrm{Bipy(cr) + acetone(I) \rightarrow solution\ A_1}; \quad \Delta_1 H^\theta \qquad (2)$$

$$\mathrm{Zn(S_2CNR_2)_2(cr) + solution\ A_1} \rightarrow \mathrm{solution\ A_2}; \quad \Delta_2 H^\theta \qquad (3)$$

$$\mathrm{Zn(S_2CNR_2)_2 \cdot bipy(cr) + acetone(I)} \rightarrow \mathrm{solution\ A_3}; \quad \Delta_3 H^\theta \qquad (4)$$

$$\mathrm{Solution\ A_2 \rightarrow solution\ A_3}; \quad \Delta_4 H^\theta \qquad (5)$$

The application of Hess' law to the series of reactions (2)–(5) gives: $\Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta$, since the final systems $A_3$ and $A_4$ are equivalent and $\Delta_4 H^\theta = 0$. By using appropriate thermochemical cycles and applying Hess' law [20], the standard enthalpies of the following reactions were obtained

$$\mathrm{Zn(S_2CNR_2)_2(g) + bipy(g)} \rightarrow \mathrm{Zn(S_2CNR_2)_2 \cdot bipy(cr)}; \quad \Delta_M H^\theta$$

$$\Delta_M H^\theta = \Delta_r H^\theta - \Delta_{cr}^{g} H^\theta[\mathrm{Zn(S_2CNR_2)_2}] - \Delta_{cr}^{g} H^\theta(\mathrm{bipy}); \quad \Delta_M H^\theta$$

$$\mathrm{Zn(S_2CNR_2)_2 \cdot bipy(cr)} \rightarrow \mathrm{Zn(S_2CNR_2)_2(cr) + bipy(g)}; \quad \Delta_D H^\theta$$

$$\Delta_D H^\theta = \Delta_{cr}^{g} H^\theta(\mathrm{bipy}) - \Delta_r H^\theta$$

$$\mathrm{Zn(S_2CNR_2)_2 \cdot bipy(g)} \rightarrow \mathrm{Zn(S_2CNR_2)_2(g) + bipy(g)}; \quad \Delta_r H^\theta$$

$$\Delta_r H^\theta(g) = -\Delta_{cr}^{g} H^\theta[\mathrm{Zn(S_2CNR_2)_2}] - \Delta_{cr}^{g} H^\theta(\mathrm{bipy}) + \Delta_r H^\theta + \Delta_{cr}^{g} H^\theta[\mathrm{Zn(S_2CNR_2)_2 \cdot bipy}].$$

From the values of $\Delta_r H^\theta$, the standard enthalpies of formation of the adducts were determined, as $\Delta_f H^\theta$(adduct)$=\Delta_r H^\theta + \Delta_f H^\theta[\mathrm{Zn(S_2CNR_2)_2}] + \Delta_f H^\theta$(bipy). The $\Delta_r H^\theta$(g) can be used to calculate the mean zinc–nitrogen bond-dissociation enthalpies, since $\langle D \rangle$ (Zn–N), is equal to $-\Delta_r H^\theta(g)/2$. Table 5 lists the thermochemical parameters of the adducts. For the determination of $\Delta_r H^\theta$(g), it was necessary to obtain the values for $\Delta_{cr}^{g} H^\theta$ of the adducts. However, all attempts to sublime these compounds were unsuccessful. Therefore, this parameter was determined by means of differential scanning calorimetry and estimative methods [6,7,12,21]. The standard enthalpies of melting (Fig. 1) as well as the heat capacities of the solid (Fig. 2) and liquid (Fig. 3) adducts were determined by DSC [21]. The standard enthalpies of vaporization were estimated by the methods of Giacolone

Table 5
Thermochemical data summary (kJ mol$^{-1}$)

| Compound | $\Delta_r H^\theta$ | $\Delta_f H^\theta$ | $\Delta_{cr}^{g} H^\theta$ | $\Delta_M H^\theta$ | $\Delta_D H^\theta$ | $\Delta_r H^\theta$(g) |
|---|---|---|---|---|---|---|
| $Zn(S_2CNEt_2)_2$(cr) | | −289.65±4.90[a] | 115±15[a] | | | |
| $Zn(S_2CNPr^n_2)_2$(cr) | | −440.68±2.85[b] | 147±2[b] | | | |
| $Zn(S_2CNBu^n_2)_2$(cr) | | −471.23±3.90[c] | 107±3[c] | | | |
| $Zn(S_2CNBu^i_2)_2$(cr) | | −526.06±3.30[d] | 283±2[d] | | | |
| $Zn(S_2CNPe^n_2)_2$(cr) | | −409±6[e] | 127±3[e] | | | |
| Bipy(cr) | | −216.40±7.40[f] | 81.93±0.33[g] | | | |
| $[Zn(S_2CNEt_2)_2\cdot$bipy](cr) | −26.19±0.49 | −99.44±8.89 | | −223±15 | 108.12±0.77 | −107±15 |
| $[Zn(S_2CNPr^n_2)_2$ bipy](cr) | −34.60±0.05 | −258.88±7.93 | | −264±2 | 116.53±0.59 | −145±3 |
| $[Zn(S_2CNBu^n_2)_2$ bipy](cr) | −26.93±0.06 | −281.76±8.37 | | −216±3 | 108.86±0.33 | −95±6 |
| $[Zn(S_2CNBu^i_2)_2$ bipy](cr) | −23.46±0.07 | −333.12±8.10 | | −338±2 | 105.39±0.34 | −275±2 |
| $[Zn(S_2CNPe^n_2)_2$ bipy](cr) | −15.74±0.04 | −208±10 | | −225±3 | 97.67±0.33 | −113±4 |

[a] [28].
[b] [12].
[c] [26].
[d] [7].
[e] See text.
[f] [22].
[g] [23].

[22], Riedel–Planck–Miller [22], and Watson [23]. The results were consistent and the mean value obtained for each compound is listed in Table 6. The heat capacities of the gaseous adducts were estimated by the method of generalized vibrational assignment [6,7,12,21–23] which resulted in the expressions (kJ mol$^{-1}$ K$^{-1}$)

For $Zn(S_2CNEt_2)_2 \cdot C_{10}H_8N_2$ :

$$C^0_{p(g)} = -0.112 + 2.414 \times 10^{-3}T - 1.054 \times 10^{-6}T^2;$$

For $Zn(S_2CNPr^n_2)_2 \cdot C_{10}H_8N_2$ :

$$C^0_{p(g)} = -0.141 + 2.629 \times 10^{-3}T - 1.263 \times 10^{-6}T^2;$$

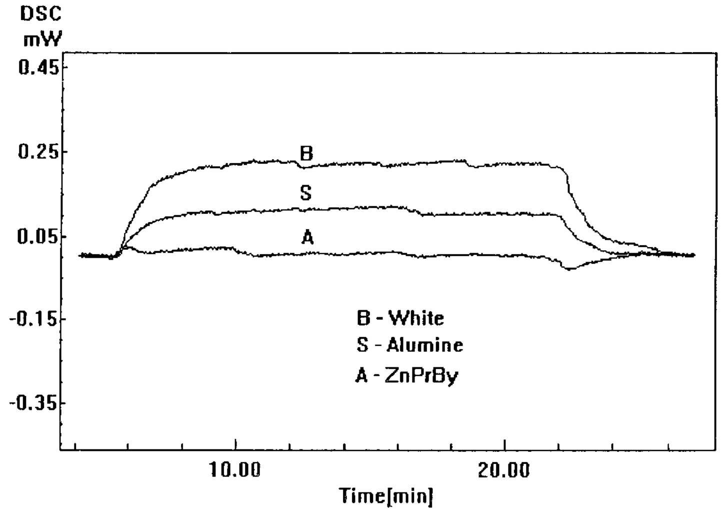

Fig. 2. Heat capacity of the $Zn(S_2CNPr^n_2)_2\cdot$bipy, in solid phase.

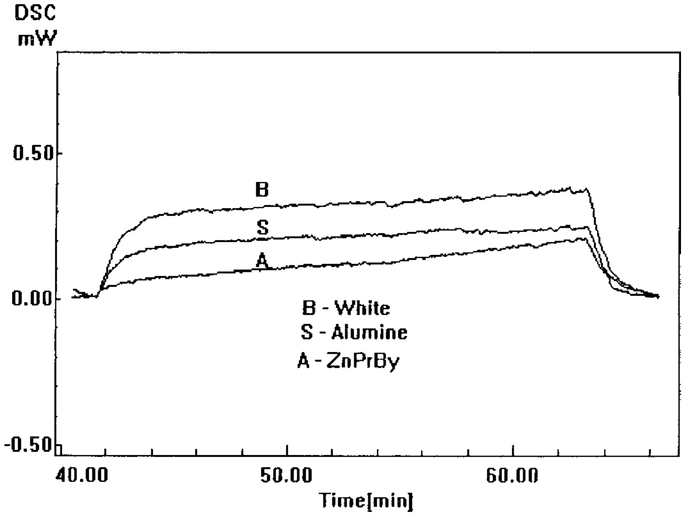

Fig. 3. Heat capacity of the $Zn(S_2CNPr^n_2)_2 \cdot bipy$, in liquid phase.

For $Zn(S_2CNBu^n_2)_2 \cdot C_{10}H_8N_2$ :

$$C^0_{p(g)} = -0.172 + 2.971 \times 10^{-3}T - 1.263 \times 10^{-6}T^2;$$

For $Zn(S_2CNBu^i_2)_2 \cdot C_{10}H_8N_2$ :

$$C^0_{p(g)} = -0.159 + 2.888 \times 10^{-3}T - 1.145 \times 10^{-6}T^2;$$

For $Zn(S_2CNPe^n_2)_2 \cdot C_{10}H_8N_2$ :

$$C^0_{p(g)} = -0.185 + 3.262 \times 10^{-3}T - 1.358 \times 10^{-6}T^2.$$

where $T$ is vaporization temperature of the compounds.

Applications of all these auxiliary data to Eq. (6) resulted in the standard enthalpies of sublimation of the adducts, Table 6

$$\Delta^{g}_{cr}H^0_m = \int_{298.15\,K}^{T_{fus}} Cp(cr)\,dT + \Delta^{l}_{cr}H^0_m + \int_{T_{fus}}^{T_{vap}} Cp(l)\,dT + \Delta^{g}_{l}H^0_m + \int_{T_{vap}}^{298.15\,K} Cp(g)\,dT \qquad (6)$$

Table 6 lists the values obtained for these thermochemical parameters. The enthalpies of formation ($\Delta_f H^{\theta}$) and sublimation ($\Delta^{g}_{cr}H^{\theta}$) of $Zn(S_2CNPe^n_2)_2$ are not found in the literature, they were calculated

Table 6
Standard molar enthalpies (kJ mol$^{-1}$), melting and vaporization temperatures (K) and heat capacities (kJ mol$^{-1}$ K$^{-1}$) for the adducts

| Compound | $Zn(S_2CNEt_2)_2 \cdot bipy$ | $Zn(S_2CNPr^n_2)_2$ bipy | $Zn(S_2CNBu^n_2)_2$ bipy | $Zn(S_2CNBu^i_2)_2$ bipy | $Zn(S_2CNPe^n_2)_2$ bipy |
|---|---|---|---|---|---|
| $\Delta^{l}_{cr}H^{\theta}$ | 51.59±0.56 | 49.46±0.81 | 50.36±0.69 | 81.46±0.91 | 34.88±0.47 |
| $\Delta^{g}_{l}H^{\theta}$ | 61.5±2.1 | 63.1±2.7 | 63.1±2.3 | 60.5±3.2 | 55.29 |
| $T_m$ | 454 | 432 | 414 | 451 | 364 |
| $T_{vap}$ | 578 | 594 | 620 | 611 | 652 |
| $Cp(cr)(T)$ | 0.065±0.004 (327) | 0.926±0.049(327) | 4.261±0.119(334) | 2.691±0.098(354) | 3.072±0.102(325) |
| $Cp_{(l)}(T)$ | 0.249±0.034 (483) | 1.054±0.076(474) | 3.581±0.132(452) | 2.899±0.104(502) | 2.317±0.099(550) |
| $Cp^{\theta}{}_{(g)}$ | 0.931±0.027(578) | 0.975±0.031(594) | 1.191±0.097(620) | 1.777±0.102(611) | 1.249±0.089(652) |
| $\Delta^{g}_{cr}H^{\theta}$ | 116.2±1.7 | 118.8±2.3 | 121.1±2.4 | 113.1±2.9 | 117.0±2.5 |
| $\Delta_f H^{\theta}(g)$ | 16.7±1.9 | −140.0±8.2 | −160.6±8.4 | −220.0±8.2 | −96.0±8.0 |
| $\langle D \rangle$ (Zn–N) | 54±8 | 78±2 | 48±2 | 138±1 | 57±2 |

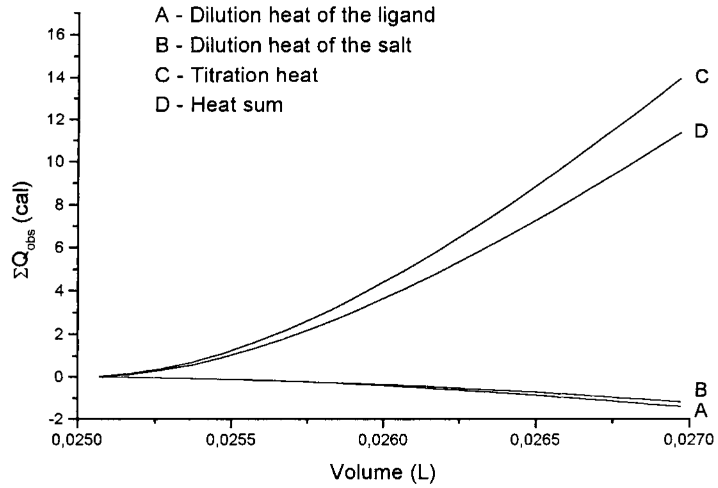

Fig. 4. Calorimetric titration of $Zn(S_2CNPr^n_2)_2$ $1\times10^{-2}$ M with bipyridine $6.257\times10^{-1}$ M in acetone.

Table 7
Thermodynamic parameters for the calorimetric titration of a solution in acetone of $Zn(S_2CNR_2)_2$ in acetone, with a solution of bipyridine

| R | ln *K* | $-\Delta H^0$ (kJ mol$^{-1}$) | $-\Delta S^0$ (J mol$^{-1}$ K$^{-1}$) | $-\Delta G^0$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| Ethyl | 1.10±0.02 | 59.27±0.92 | 208±4 | 2.73 |
| *n*-Propyl | 1.15±0.03 | 61.72±1.87 | 216±5 | 2.86 |
| *n*-Butyl | 1.18±0.04 | 68.96±1.69 | 247±5 | 2.85 |
| iso-Butyl | 1.06±0.01 | 72.14±1.96 | 251±3 | 2.56 |
| *n*-Pentyl | 1.09±0.02 | 65.23±1.02 | 227±3 | 2.70 |

by a group contribution method [24,25] from the values for $Zn(S_2CNBu^n_2)_2$. The values of the mean zinc–nitrogen bond-dissociation enthalpies [26], $\langle D\rangle$(Zn–N), increase in the sequence: $Bu^n<Et<Pe^n<Pr^n<Bu^i$.

Typical calorimetric titration curves of Zn(II) dialkyldithiocarbamate with bipyridine in acetone as a solvent, are shown in Fig. 4. The net heat is obtained from the algebraic sum of the heat of titration and the heats of dilution. By plotting the net heat versus the added volumes, it is possible to calculate the $\Delta H^0$ and $K$ values of the interaction [27]. From these last values, the $\Delta G^0$ and $\Delta S^0$ values were calculated (Table 7).

## 4. Discussion

$K$ and consequently $\Delta G^0$ values vary very little with the R-group bonded in the anion dialkyldithiocarbamate. The entropy change ($\Delta S^0$) increases as the alkyl group R gets longer. The enthalpy change ($\Delta H^0$) increases in the sequence: $Et<Pr^n<Pe^n<Bu^n<Bu^i$. Adduct stability (ln *K*) is low compared with the same metal ion adducts because of the $\Delta S^0$ large, negative values.

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