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THERMOCHEMICAL PARAMETERS OF DIMETHYL AND DI-*ISO*-PROPYL DITHIOCARBAMATE COMPLEXES OF PALLADIUM(II)

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Abstract

The standard molar enthalpy of formation of crystalline dialkyldithiocarbamate chelates, $[\mathrm{Pd}(\mathrm{S_2CNR_2})_2]$, with R=$\mathrm{CH_3}$ and i-$\mathrm{C_3H_7}$, was determined through reaction-solution calorimetry in 1,2-dichloroethane, at 298 K. Using the standard molar enthalpies of formation of the gaseous chelates, the homolytic (526±18 and 666±10) and heterolytic (2693±18 and 2957±10 kJ $\mathrm{mol^{-1}}$) mean enthalpies of palladium–sulphur bond dissociation were calculated.

Keywords: calorimetry, dialkyl dithiocarbamate, enthalpy, palladium

Introduction

In the last decade, the study of metallic dithiocarbamate complexes and similar compounds had a progressive development, due to the arisement of new analytical techniques [1–5].

Thermochemical data in literature, concerning dithiocarbamates, are essentially originated from techniques such as: thermogravimetry, differential thermal analysis, differential scanning calorimetry, chromatography in gaseous phase, mass spectrometry and in smaller extension, solution calorimetry and thermometric titulation [1–8].

This publication focuses on the determination of thermochemical data for chelates of Pd(II) dialkyldithiocarbamate. These results are important in the understanding of the effect of the alkyl chain length attached to the nitrogen of the ligand.

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Experimental

The ammonium chloride salts, R_2NH_2Cl, and dialkylammonium dialkyldithiocarbamate, $R_2NH_2S_2CNR_2$, were synthesized with R=CH_3 and i-C_3H_7. Their chemical analysis were in agreement with their formulation. The dialkyldithiocarbamate of palladium(II) complexes $[Pd(S_2CNR_2)_2]$, with R=CH_3 and i-C_3H_7 were synthetized from the direct reaction of $PdCl_2$ with corresponding amine and carbon disulphide in acetone.

Microanalysis (C, H, N) were carried out with a Perkin Elmer elemental analyser. Infrared spectra were recorded as KBr pellets on a BOMEM spectrophotometer, model MB-102. Thermogravimetric (TG) curves were obtained using a Shimadzu thermobalance, model TGA-50, at a heating rate of 10°C min^{-1} in a dynamic atmosphere of dry nitrogen flux of 0.83 mL s^{-1} and mass spectra of the ligand and chelates were obtained on a Hewlett–Packard spectrometer, model 5988A, with an ionization energy of 70 eV, at 523 K.

All solution calorimetric determinations were carried out in an LKB 8700-1 isoperibolic precision calorimeter system as described before [9]. The enthalpies of decomposition of the chelates were determined in a Shimadzu differential scanning calorimeter, model DSC-50, at a heating rate of 10ºC min^{-1}, purged with dry nitrogen [9, 10].

Results and discussion

The CHN elemental analysis of the complexes, $Pd(S_2CNR_2)_2$, with R=CH_3 and i-C_3H_7, are in good agreement with the expected values, according to Table 1.

Table 1 Main absorptions in the infrared spectra (cm^{-1}) and mass percentage analysis (%) for complexes

Complexes	ν(C–S)	ν(C=N)	ν(Pd–S)	C	N	H
$Pd(S_2CNMe_2)_2$	966.4	1543.4	162.0	20.83(21.15)	8.10(8.05)	3.50(3.61)
$Pd(S_2CNPr^i_2)_2$	940.3	1494.5	160.0	36.62(37.35)	6.10(6.22)	6.16(6.68)

The thermogravimetric curves showed mass loss before the melting, for all chelates. The thermogravimetric curves resembled ligand one, which lose all mass in only one stage. This implies in a chelate decomposition occurring in solid phase. For palladium complexes, $Pd(S_2CNMe_2)_2$ and $Pd(S_2CNPr^i_2)_2$, complete mass loss occurred in only event, in the ranges 295.60–416.63 and 304.30–402.58ºC, respectively, as shown in the TG/DSC curves, presented in Fig. 1.

Results of infrared spectroscopy are presented in Table 1 and Fig. 2. The νCN band assumes a double-band character which is reflected in the appearance of a stretching band shifted to a higher frequency. For all complexes, the frequency of this band is higher than the respective ligand one. On the other hand, a decrease in the frequency of the νCS stretching band is observed and an isolated band near 1000 cm^{-1} indicates that the ligand is bonded to metal in a bidentated manner [11]. The mass

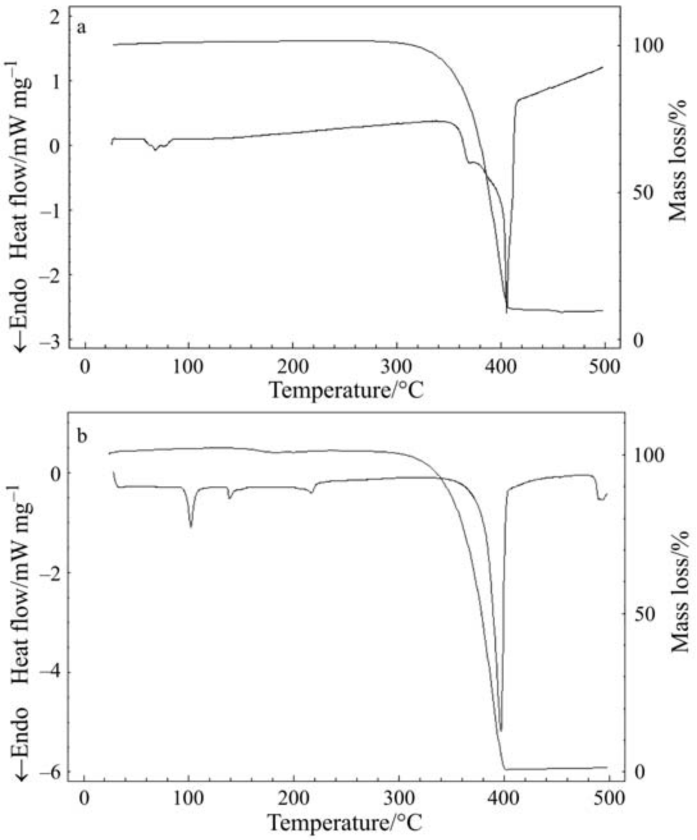

Fig. 1 TG/DSC curves of the a – [Pd(S_2CNMe_2)$_2$] and b – [Pd($S_2CNPr^i_2$)$_2$] complexes

spectra of the complexes (Table 2) indicated the presence of the parent ions with the following stability order: Pd(S_2CNMe_2)$_2$>Pd($S_2CNPr^i_2$)$_2$.

Table 2 Main mass fragments observed for complexes

Fragments	Pd(S_2CNMe_2)$_2$		Pd($S_2CNPr^i_2$)$_2$	
	m/*e*	*l*/%	*m*/*e*	*l*/%
[ML_2]$^+$	346	91.66	459.1	33.16
[ML]$^+$	226	47.86	282.0	81.04
[L]$^+$	120	6.91	176.0	23.89
[R_2NCS]$^+$			144.0	31.81
[RNHCS]$^+$	73	18.31	102.0	57.13
[R_2N]$^+$			100.0	73.24
[H_2NCS]$^+$			60.0	20.14

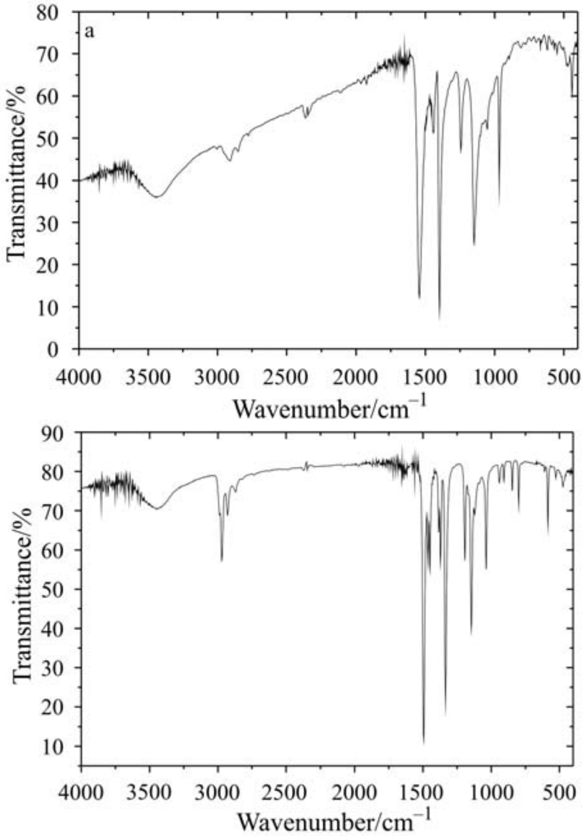

Fig. 2 Infrared spectra of the a – $[Pd(S2CNMe_2)_2]$ and b – $[Pd(S_2CNPr^i_2)_2]$ complexes

The standard molar enthalpy of reaction, $\Delta_r H^0_m$, was obtained at 298 K, from the reaction-solution enthalpies, $\Delta_i H^0_m$, of each reagent and product dissolved sequentially in 1,2-dichloroethane (Table 3). A strict control of stoichiometry was maintained, for the following general reaction [5–8]:

$$PdCl_2(cr)+2NH_2R_2S_2CNR_2(cr)\rightarrow Pd(S_2CNR_2)_2(cr)+2NH_2R_2Cl(cr);\Delta_r H^0_m \quad (1)$$

The standard molar enthalpy for each reaction was calculated from these tabulated values, applying a convenient thermochemical cycle. Individual enthalpies' values used in the calculation are listed in Table 4.

The standard molar enthalpies of formation of the crystalline chelates, shown in Table 4, were determined from $\Delta_r H^0_m$ and the respective standard molar enthalpies of formation of palladium chloride [12], ligands [17, 18] and ammonium chlorides [13, 14], using expression (1). The auxiliary data are listed in Table 5.

Table 3 Standard molar enthalpies (kJ mol^{-1}) of solution-reaction, at 298 K

Reactant	Solvent	Solution	$\Delta_r H_m^0$ / kJ mol^{-1}
$2Me_2NH_2S_2CNMe_2$ (*cr*)	1,2-dichloroethane	A_1	47.1±0.9
$PdCl_2$ (*cr*)	A_1	A_2	22.1±2.1
$Pd(S_2CNMe_2)_2$ (*cr*)	1,2-dichloroethane	A_3	9.1±0.4
$2Me_2NH_2Cl$ (*cr*)	A_3	A_4	4.3±0.2
$2Pr^i_2NH_2S_2CNPr^i_2$ (*cr*)	1,2-dichloroethane	C_1	38.5±2.0
$PdCl_2$ (*cr*)	C_1	C_2	20.8±2.0
$Pd(S_2CNPr^i_2)_2$ (*cr*)	1,2-dichloroethane	C_3	28.4±2.0
$2Pr^i_2NH_2Cl$ (*cr*)	C_3	C_4	12.3±0.6

Table 4 Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ mol^{-1} K^{-1}) and temperatures (K) for the chelates

Parameters	$Pd(S_2CNMe_2)_2$	$Pd(S_2CNPr^i_2)_2$
$\Delta_r H_m^0$	56±2	19±3
$\Delta_f H_m^0$ (*cr*)	125±15	–178±5
$\Delta_{cr}^g H_m^0$	189.8±0.9	187±1
$\Delta_f H_m^0$ (*g*)	315±15	10±5
$\Delta_{ho} H_m^0$	526±18	666±10
$\Delta_{he} H_m^0$	2693±18	2957±10
$\langle D \rangle$ (Pd–S)	131±18	167±10
$\langle D' \rangle$ (Pd–S)	673±18	739±10

Table 5 Auxiliary data

Species	$\Delta_f H_m^0$/kJ mol^{-1}	Reference
$PdCl_2$ (*cr*)	–198.70±3.08	[12]
$Me_2NH_2S_2CNMe_2$ (*cr*)	–144.00±6.4	[17]
Me_2NH_2Cl (*cr*)	–278.00±7.04	[13]
$Pr^i_2NH_2S_2CNPr^i_2$ (*cr*)	–349.6±1.3	[18]
$Pr^i_2NH_2Cl$ (*cr*)	–350.77±0.15	[14]
Pd (*g*)	378.20±0.88	[12]
Pd^{2+} (*g*)	3069.40±1.76	[12]
$Me_2NCS_2^{\cdot}$ (*g*)	231.30±4.45	[17]
$Me_2NCS_2^{-}$ (*g*)	–30.76±4.45	this work
$Pr^i_2NCS_2^{\cdot}$ (*g*)	149.10±4.35	[18]
$Pr^i_2NCS_2^{-}$ (*g*)	–51.41±4.35	this work

The standard molar enthalpies of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}$, were determined by means of differential scanning calorimetry and estimative methods [5–8, 15, 17, 18].

The complexes [Pd(S_2CNR_2)$_2$, *cr*], R=C_2H_5, *n*-C_3H_7, *n*-C_4H_9 and *i*-C_4H_9, decompose in liquid phase [16], while complexes with R=CH_3 and *i*-C_3H_7 decompose in solid phase, not being possible to calculate the sublimation enthalpies, according to Eq. (2).

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0}=\int_{298.15\,\mathrm{K}}^{T_{\mathrm{fus}}}C_{\mathrm{p}}(cr)\mathrm{d}T+\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{0}+\int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}}C_{\mathrm{p}}(l)\mathrm{d}T+\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{0}+\int_{T_{\mathrm{vap}}}^{298.15\,\mathrm{K}}C_{\mathrm{p}}(g)\mathrm{d}T \qquad (2)$$

Silva *et al.* [17, 18] considered that standard molar enthalpy of ligand decomposition is equal to its sublimation apparent enthalpy. Literature data [17, 18] for standard molar enthalpies of ligand decomposition are: 189.80±0.91 and 187.70±1.0 kJ mol^{-1} for R=CH_3 and *i*-C_3H_7, respectively.

Standard molar enthalpy of sublimation of the complexes [Pd(S_2CNR_2)$_2$, *cr*], where R=CH_3 and *i*-C_3H_7, may be considered as being equal to standard molar enthalpy of sublimation of its ligands [19]. To calculate standard molar enthalpies of chelates formation in gaseous phase and of dissociation energy of the bonding Pd–S, according to homolytic and heterolytic parameters, it was necessary to use values of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{\cdot}S_2CNR_2$, *g*) and $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{-}S_2CNR_2$, *g*). These values were calculated using experimental data of standard molar enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($HS_2CNR_2$, *g*) where R=CH_3 and *i*-C_3H_7.

According to standard molar enthalpies of dissociation of the bonding (S–H) of different compounds, Benson [20] determined that D_{m}(S–H)=385.0±5.0 kJ mol^{-1}. Using the equation $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{\cdot}S_2CNR_2$, *g*)=$D_{\mathrm{m}}$(S–H)+$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($HS_2CNR_2$, *g*)–$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{\cdot}$H, *g*), where $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{\cdot}$H, *g*)=218.00±0.01 kJ mol^{-1} [17, 18], standard molar enthalpies of radical formation in gaseous phase were calculated ($^{\cdot}S_2CNR_2$, *g*). To calculate standard molar enthalpies of anions formation in gaseous phase ($^{-}S_2CNR_2$, *g*), the equation $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{-}S_2CNR_2$, *g*)=$E_{\mathrm{L}}$+$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($^{\cdot}S_2CNR_2$, *g*)+$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}$($e^{-}$) was used, where E_{L}= –200.42 ±0.05 kJ mol^{-1} and $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{0}(e^{-})=0$. The values of standard molar enthalpies of formation and dissociation energies of the complexes, using homolytic and heterolytic parameters, are presented in Table 4.

Auxiliary data, listed in Table 5, enable the calculation of the mean enthalpy of palladium–sulphur bond [5–8, 10, 16] for homolytic, <*D*> (Pd–S)=$\Delta_{\mathrm{ho}}H_{\mathrm{m}}^{0}/4$ and heterolytic parameters, <*D'*> (Pd–S)=$\Delta_{\mathrm{he}}H_{\mathrm{m}}^{0}/4$, whose values are listed in Table 4.

The results presented in Table 4 <*D*> (Pd–S) and <*D'*> (Pd–S) show values for complexes [Pd(S_2CNR_2)$_2$], with R=CH_3 and *i*-C_3H_7. These results indicate that the isopropyl complexes are more stable than methyl ones. Comparing to literature data, it may be observed that stability increases with increase of linear carbon chain. When ramification is present, stability decreases in relation to a chain with the same number of carbon atoms [16].

Conclusions

In this work, thermochemical parameters for complexes [Pd(S_2CNR_2)$_2$], with R=CH_3 and *i*-C_3H_7 were determined. It may be concluded that the bonding metal–ligand is bidentated, according to infrared spectroscopy results. Mass spectrometry indicate that in this case, the methyl complex is more stable than isopropyl one. On the other hand, dissociation energy of the bonding palladium–sulphur indicates that isopropyl complex is more stable than methyl one. Literature data indicate that, according to dissociation energy, stability increases with increase of linear carbon chain. When ramification is present, stability decreases.

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