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THERMOCHEMICAL PARAMETERS AND CALCULATIONS AB-INITIO OF THE BISDIMETHYLDITHIOCARBAMATE ZINC(II) COMPLEX

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The standard molar enthalpy of formation of crystalline bisdimethyldithiocarbamate zinc(II) complex, $Zn[S_2CN(CH_3)_2]_2$ was determined through reaction–solution calorimetry in acetone, at 298 K. Using the standard molar enthalpy of formation of the gaseous chelate, the homolytic (-619.78 ± 8.95 kJ mol^{-1}) and heterolytic (-2747.71 ± 8.95 kJ mol^{-1}) mean enthalpies of zinc–sulphur bond dissociation were calculated. The investigation on the electronic structure involved the use of molecule orbital calculations.

Introduction

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

The thermal properties of some metal dithiocarbamate complex [3–5, 8] together with the determination of the standard molar enthalpies of formation of zinc, cadmium and palladium chelates through reaction–solution calorimetry were used to estimate the homolytic and heterolytic metal–sulphur bond enthalpies. Recently, the kinetic parameters of the thermal decomposition of zinc(II) dialkyldithiocarbamate complex was studied [9].

Molecule orbital calculation was done to simulate the variation of the electronic structure. Gaussian98 package was used for these calculations.

Experimental

The ammonium chloride salt, $(CH_3)_2NH_2Cl$ and dimethylammonium dimethyldithiocarbamate, $(CH_3)_2NH_2S_2CN(CH_3)_2$ were synthesized. Their elemental analyses were in agreement with the data calculated from their chemical formulas. The bisdi-

methyldithiocarbamate zinc(II) complex $Zn[S_2CN(CH_3)_2]_2$ was synthetized from the direct reaction of $ZnCl_2$ with dimethylamine and carbon disulphide in acetone.

The microanalyses (C, H, N) were carried out with a PerkinElmer elemental analyser. Infrared spectra were recorded in KBr pellets using a Bomem model MB – 102 spectrometer. TG curves were obtained using Shimadzu model TGA-50 thermobalance, at a heating rate of 10 K min^{-1} in a dynamic nitrogen atmosphere with a flow rate of 0.83 mL s^{-1}. Mass spectra of the ligand and chelates were obtained using a Hewlett-Packard model 5988A mass spectrometer, with an ionization energy of 70 eV at 523 K.

All solution calorimetric determination were carried out in an LKB 8700-1 isoperibolic precision calorimeter system as described before [10]. Decomposition of the chelates were determined in a Shimadzu model DSC-50, Differential Scanning Calorimeter; at a heating rate of 10 K m^{-1}, purged with dry nitrogen [10, 11].

In this work, we obtained the structural properties of the bisdimethyldithiocarbamate zinc(II) complex using calculations ab-initio in level Hartree–Fock–Roothaan. We have performed all the calculations by using the Gaussian98 software [12], with effective core potential and double-ξ basis set, LanL2DZ [13] on Zn and 6-31G(*) [14] on H, N, S and C.

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Results and discussion

The CHN elemental analysis of the complex, $Zn[S_2CN(CH_3)_2]_2$ are in a good agreement with the calculated results. The main absorptions in the infrared spectra (cm^{-1}) are: $\nu(C–S)=973.30$, $\nu(C=N)=1522.99$ and $\nu(Zn–S)=163.30$.

The melting point of the complex is 253.1°C, obtained by DSC. By the comparison of TG and DSC curves is well visible that the mass loss process starts before the melting of the chelate, i.e. in its solid-state. The TG curve indicates that the ligand is released in one step. For zinc complex, $Zn[S_2CN(CH_3)_2]_2$, complete mass loss took place in one step between 244–340°C, as it is shown in the TG/DSC curves (Fig. 1).

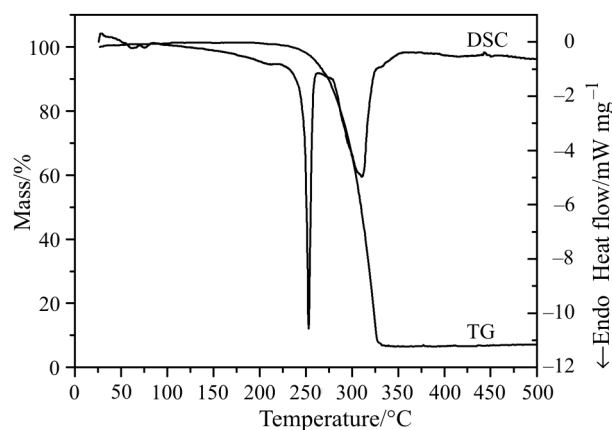**Fig. 1** TG/DSC curves of the $Zn[S_2CN(CH_3)_2]_2$ complex

Fig. 2 Infrared spectra of the $Zn[S_2CN(CH_3)_2]_2$ complex

Results of infrared spectroscopy experiments are presented in Fig. 2. The νCN (1522.99 cm^{-1}) band assumes a double-band character, which is reflected in the appearance of a stretching band shifted to a higher frequency. The frequency of this band is higher than the respective ligand's band has. On the other hand, a decrease in the frequency of the νCS (973.30 cm^{-1}) stretching band is observed and an isolated band near 1000 cm^{-1} indicates that the ligand is bonded to metal in a bidentated manner [15]. The mass spectra of the complex, $Zn[S_2CN(CH_3)_2]_2$ indicated the presence of the molecular ion, which relative intensity is 100% (parent peak), suggesting a high stability.

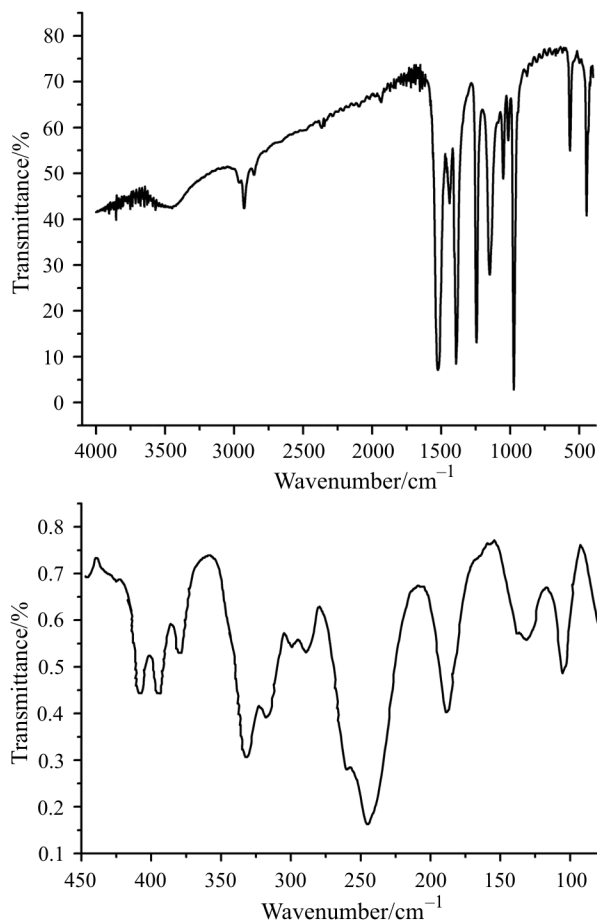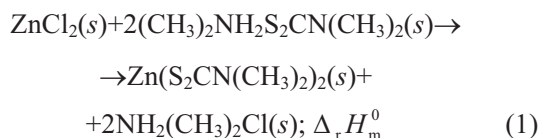$\Delta_r H_m^0$, the standard molar enthalpy of reaction was obtained at 298 K, from the reaction–solution enthalpies. This value for each reagent and product dissolved in acetone are given in Table 1. A strict stoichiometric control was maintained, following the general reaction [5–8]:

$$ZnCl_2(s)+2(CH_3)_2NH_2S_2CN(CH_3)_2(s)\rightarrow$$
$$\rightarrow Zn(S_2CN(CH_3)_2)_2(s)+$$
$$+2NH_2(CH_3)_2Cl(s); \Delta_r H_m^0 \qquad (1)$$

The standard molar enthalpy for each reaction was calculated from these values, applying a convenient thermochemical cycle. Individual enthalpy values used for the calculation are listed in Table 2.

Table 1 Standard molar enthalpies of solution–reaction, at 298 K

Reactant	Solvent	Solution	$\Delta_t H_m^0$ /kJ mol^{-1}
$2(CH_3)_2NH_2S_2CN(CH_3)_2(s)$	acetone	A_1	10.68±0.35
$ZnCl_2(s)$	A_1	A_2	−37.48±0.56
$Zn(S_2CN(CH_3)_2)_2(s)$	acetone	A_3	26.86±2.12
$2(CH_3)_2NH_2Cl(s)$	A_3	A_4	15.58±1.11

The standard molar enthalpy of formation of the crystalline chelate were determined from $\Delta_r H_m^0$ and the respective standard molar enthalpies of formation of zinc chloride [16], ligand [17, 18] and ammonium chloride [19, 20], using expression (1) are given in Table 2, while the auxiliary data are listed in Table 3.

Table 2 Standard molar enthalpies for the chelate

Parameters	kJ mol^{-1}
$\Delta_r H_m^0$	−69.24±2.49
$\Delta_f H_m^0(s)$	−216.25±7.72
$\Delta_s^g H_m^0$	189.80±0.91
$\Delta_f H_m^0(g)$	−26.45±7.77
$\Delta_{ho} H_m^0$	−619.78±8.95
$\Delta_{he} H_m^0$	−2747.71±8.95
$<D>$(Zn–S)	154.95±8.95
$<D'>$(Zn–S)	686.93±8.95

Table 3 Auxiliary data

Species	$\Delta_f H_m^0$ /kJ mol^{-1}	Reference
$ZnCl_2(s)$	−415.05±0.02	[16]
$(CH_3)_2NH_2S_2CN(CH_3)_2(s)$	−144.00±6.40	[17]
$(CH_3)_2NH_2Cl(s)$	−278.00±7.04	[19]
$Zn^\bullet(g)$	130.73±0.01	[16]
$Zn^{2+}(g)$	2782.78±0.03	[16]
$(CH_3)_2NCS_2^\bullet(g)$	231.30±4.45	[17]
$(CH_3)_2NCS_2^-(g)$	−30.76±4.45	[22]

The standard molar enthalpy of sublimation, $\Delta_s^g H_m^0$ were determined using DSC and estimation methods [5–8, 17, 18, 21].

The complex $Zn[S_2CN(CH_3)_2]_2(s)$ decomposes in solid phase. Consequently it was not possible to calculate the sublimation enthalpy, according to Eq. (2).

$$\Delta_s^g H_m^0 = \int_{298.15\,K}^{T_{fus}} C_p(s)dT + \Delta_s^l H_m^0 +$$
$$+ \int_{T_{fus}}^{T_{vap}} C_p(l)dT + \Delta_l^g H_m^0 + \int_{T_{vap}}^{T_{298.15\,K}} C_p(g)dT \quad (2)$$

Botelho *et al*. reported that the standard molar enthalpy of ligand decomposition is equal to its apparent enthalpy of sublimation [22]. Literature data [17, 18] for standard molar enthalpies of ligand decomposition are 189.80±0.91 kJ mol^{-1}. Standard molar enthalpy of sublimation of the complex $Zn[S_2CN(CH_3)_2]_2(s)$ can be considered as being equal to the standard molar enthalpy of sublimation of its ligand [23]. According to homolytic and heterolytic parameters for the calculation of the standard molar

enthalpies of chelate formation in gaseous phase and the dissociation energy of the Zn–S binding was necessary to use the $\Delta_f H_m^0[^\bullet S_2CN(CH_3)_2, g]$ and $\Delta_f H_m^0[^- S_2CN(CH_3)_2, g]$ values, which were calculated from the experimental data of standard molar enthalpies of formation $\Delta_f H_m^0[HS_2CN(CH_3)_2, g]$.

According to the standard molar enthalpies of dissociation of the S–H binding of different compounds, Benson [24] determined that $\Delta_m(S–H)=385.0±5.0$ kJ mol^{-1}. Using the equation

$$\Delta_f H_m^0[^\bullet S_2CN(CH_3)_2, g] =$$
$$= \Delta_m(S-H) + \Delta_f H_m^0[HS_2CN(CH_3)_2, g] -$$
$$\square \Delta_f H_m^0(H^\bullet, g),$$

where $\Delta_f H_m^0(H^\bullet, g) = 218.00±0.01$ kJ mol^{-1} [17, 18], standard molar enthalpy of radical formation in gaseous phase were calculated [$^\bullet S_2CN(CH_3)_2, g$]. To calculate the standard molar enthalpies of formation in gaseous phase [$^- S_2CN(CH_3)_2, g$], the equation

$$\Delta_f H_m^0[^- S_2CN(CH_3)_2, g] =$$
$$= E_L + \Delta_f H_m^0[^- S_2CN(CH_3)_2, g] + \square \Delta_f H_m^0(e^-)$$

was used, where $E_L=-200.42±0.05$ kJ mol^{-1} and $\Delta_f H_m^0(e^-) = 0$. The values of standard molar enthalpies of formation and dissociation energies of the complex, using homolytic and heterolytic parameters, are presented in Table 2.

Auxiliary data, listed in Table 3, enable the calculation of the mean enthalpy of zinc–sulphur bond [5–8, 10, 11] for homolytic, $<D>(Zn-S) = \Delta_{ho} H_m^0 / 4$, and heterolytic parameters, $<D'>(Zn-S) = \Delta_{he} H_m^0 /4$, whose values are listed in Table 2.

Several calculations have been performed to obtain a structure belonging to lower energy. The XCrysDen program was used to develop the structure (Fig. 3) with lower energy [25]. The sulfur atoms complexed with the zinc atom and formed a diagonal angle of 90° according to Fig. 3. Figure 4 illustrates the plot of energy *vs*. DOS. The data originated from the optimized structure by the Gaussian98 software. On the top of the valence band to the HOMO and the
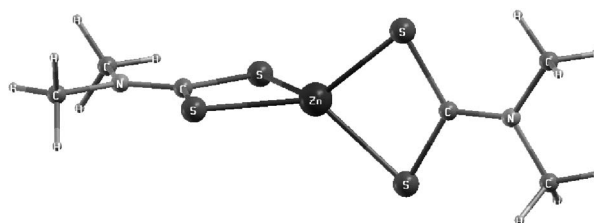

Fig. 3 Schematic representation of the cluster of $Zn[S_2CN(CH_3)_2]_2$ optimized. Spheres indicate the atomic positions
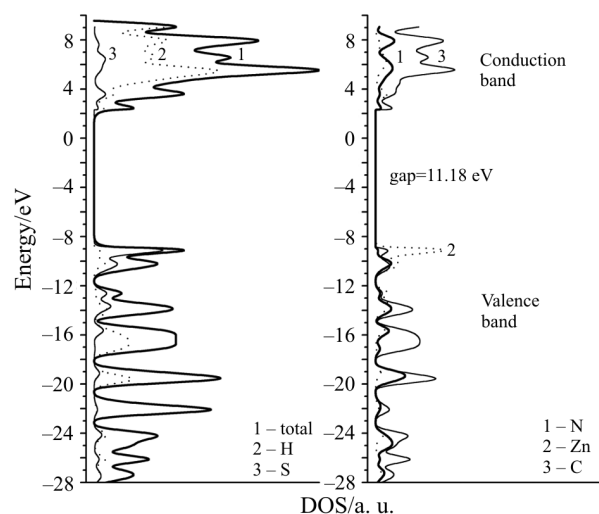
Fig. 4 Density of states for the atoms H, S, N, Zn, C and total density for the investigated cluster

bottom of the conduction band to the LUMO of the studied system.

Conclusions

Thermochemical parameters for complex $Zn[S_2CN(CH_3)_2]_2$ were determined in this work. It may be concluded that the metal-ligand binding is bidentated, according to infrared spectroscopy results. Mass spectroscopy results indicate that methyl complex is very stable.

Observing Fig. 4 it can be noticed that the complex present an insulator character, gap=11.18 eV, and the HOMO displays the prominence of the orbitals from the sulfur and zinc atoms, which suggests a covalent character interaction, since both atoms present several energy levels at a region in the vicinity of the HOMO.

Acknowledgements

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