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Thermochemical Parameters of Mercury(II) Chelates Involving Dimethyl and Di-isopropyl Dithiocarbamates

J. R. Botelho,[†,⊥] C. D. Pinheiro,[‡] A. D. Gondim,[†] P. O. Dunstan,[*,§] I. M. G. Santos,[†] and A. G. Souza[†]

[†]Departamento de Química, CCEN, Universidade Federal da Paraíba, Campus I, 58059-900, João Pessoa, Paraíba, Brazil

[‡]Unidade Acadêmica de Ciências Exatas e da Natureza, CFP, Universidade Federal de Campina Grande, 58900-000, Cajazeiras, Paraíba, Brazil

[§]Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, 13084-971, Campinas, São Paulo, Brazil

Ⓢ *Supporting Information*

ABSTRACT: The standard molar enthalpies of formation of crystalline dialkyldithiocarbamate chelates of mercury(II) were determined by using reaction-solution calorimetry. Two different complexes were studied: $Hg(S_2CNR_2)_2$ with R = CH_3 (Me) and i-C_3H_7 (Pr^i). The enthalpies of formation for the mercury complexes were determined in 1,2-dichloroethane at 298 K. The hemolytic and heterolytic mean enthalpies of dissociation of the Hg−S bonds were calculated by using the standard molar enthalpy of the gaseous chelates.

INTRODUCTION

Thermodynamic data in the literature concerning dithiocarbamates mainly originate from measurements that use techniques such as: thermogravimetry, differential thermal analysis and differential scanning calorimetry, chromatography in the gaseous phase, mass spectrometry, and some data from solution calorimetry and thermometric titration. Recently several articles have been published mentioning the synthesis and characterization of dithiocarbamate complexes.[1−8]

The hemolytic and heterolytic metal−sulfur bond enthalpies have been determined by using the thermal properties of some metal dithioicarbamate complexes,[3−8] together with the determination of the standard molar enthalpies of formation of the dialkyldithiocarbamates of zinc(II), cadmium(II), mercury(II), and palladium(II) by using reaction-solution calorimetry. The stability of the complexes of palladium increases with the increase in size of the linear carbon chain and decreases with the alkyl substitution on it.[7,8]

The synthesis of a new dithiocarbamate ligand and its complexes with copper(II), nickel(II) and palladium(II) as well as, their physicochemical characterization has been reported. Their thermal decomposition was continuous and the stabilities of the complexes were greater than that of the ligand.[9]

The single crystal structure of the complex $Cd_2((S_2CN(C_3H_7)_2)_4$ was determined by X-ray diffraction. The binuclear molecule is centrosymmetric, and its central eight-membered tricyclic moiety ($Cd_2S_4C_2$) has a chair conformation.[10]

Complexes of cadmium(II) dithiocarbamates with benzyl or methylferrocene ligands were synthesized, and the thermal behaviors were determined by using thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques. IR spectra of the complexes suggest bidentate coordination between the dithiocarbamate ligand with zinc, palladium, or other cation ions.[6−8,11] The structures of the complexes of zinc(II) dithiocarbamate were determined by the X-ray diffraction of single crystals. The mesomeric effect of dithiocarbamate groups and the inductive effect of alkyl substituents were also studied. When the metal is zinc instead of cadmium, the complex stabilized has a boat conformation.[12]

EXPERIMENTAL SECTION

The salts ammonium chloride (R_2NH_2Cl) and dialkylammonium dialkyldithiocarbamate ($R_2NH_2S_2CNR_2$) were synthesized with R = Me and Pr^i. Elemental analysis confirmed the general formula. Complexes of dialkyldithiocarbamates of mercury(II) ($Hg(S_2CNR_2)_2$) were synthesized from the direct reaction of $HgCl_2$ with the corresponding amine and carbon disulfide in acetone, using a two-neck flask of 500 mL, stirring, and a dry gaseous nitrogen flow.

The elemental analysis (C, H, N) of the complexes were carried out by using a Perkin-Elmer PE-2400 analyzer. Infrared spectra were recorded with samples in a KBr matrix using a Bomem spectrophotometer MB-102. TG curves were obtained in a dynamic nitrogen atmosphere (flow rate of 0.83 $mL \cdot s^{-1}$) using a Shimadzu TGA-50 thermobalance, with a heating rate of 10 $K \cdot min^{-1}$. The mass spectra of ligands and complexes were obtained by using a Hewlett-Packard 5988A spectrometer, with an ionization energy of 70 eV at 523 K.

All solution calorimetric measurements were carried out in an LKB 8700-1 precision calorimeter, by the broken ampule method, as previously described.[8] Thermal decomposition of the complexes were determined by using a Shimadzu differential scanning DSC-50 calorimeter, with a heating rate of 10 $K \cdot min^{-1}$ and dry nitrogen as the purged gas.

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Table 1. Analytical Data of the Complexes

complex	%C		%N		%H	
	calcd	exp.	calcd	exp.	calcd	exp.
$Hg(S_2CNMe_2)_2$	15.21	15.33	6.15	6.35	2.59	2.72
$Hg(S_2CNPr^i{}_2)_2$	31.21	31.38	4.24	4.06	5.08	5.06

Table 2. Main IR Spectral Data (cm^{-1}) of the Complexes

complex	$\nu_{(C=N)}$	$\nu_{(C-S)}$	$\nu_{(Hg-S)}$
$Hg(S_2CNMe_2)_2$	1506	965	163
$Hg(S_2CNPr^i{}_2)_2$	1480	935	160

RESULTS AND DISCUSSION

The results obtained for the elemental analysis (C, H, N) of the complexes are in good agreement with the percentages calculated from the general formula proposed. Table 1 presents theoretical and calculated results.

Infrared Spectra. The extracted infrared spectral data of the complexes are presented in Table 2. The bands attributed to the stretching $\nu_{C=N}$ are found at approximately 1500 cm^{-1}, confirming the double bond character of the CN bond. The band due to the stretching ν_{CS} is shifted to lower frequencies in relation to the free ligands. A band observed at 1000 cm^{-1} is indicative that the ligands are bonded to the metal ion in a bidentate coordination.[13]

Thermal Studies. The thermogravimetric curves of the complexes show the loss of mass before melting. This means that the complexes decompose in the solid state. For $Hg(S_2CNMe_2)_2$ the completed loss of mass occurred in two steps: from (265 to 351) K and from (351 to 482) K. For $Hg(S_2CNPr^i{}_2)_2$ the loss of mass occurred from (228 and 326) K and from (326 to 408) K. The second complex, that has alkyl substitution on the carbon chain, is less thermally stable than the former complex.

Mass Spectra. The mass spectra of the complexes showed the presence of the parent ions with the stability order: $Hg(S_2CNMe_2)_2 > Hg(S_2CNPr^i{}_2)_2$. The relative intensity of the molecular ion peaks are: 64.10 and 5.93, respectively. This shows that the stability of the complexes in the gaseous phase is the same as the stability observed in the thermal decomposition.

Calorimetric Measurements. The standard reaction enthalpy for one mole of complex was obtained at 298 K by using reaction-solution calorimetry. For this, one and two moles of each reagent or product were dissolved sequentially in 1,2-dichloroethane. The enthalpy values are given in Table 3. A very strict control of stoichiometry was maintained according to the general reaction:

$$HgCl_{2(cr)} + 2R_2NH_2S_2CNR_{2(cr)} \rightarrow Hg(S_2CNR_2)_{2(cr)} + 2NH_2R_2Cl_{(cr)}; \quad \Delta_rH^\theta{}_m \qquad (1)$$

The standard molar enthalpy of reaction for each reaction ($\Delta_rH^\theta{}_m$) in $kJ \cdot mol^{-1}$ were calculated by using the values obtained for the solution enthalpies in Table 3 and an appropriate thermochemical cycle.

The standard molar enthalpies of formation of the crystalline chelates were determined from the $\Delta_rH^\theta{}_m$ values and the respective standard molar enthalpies of formation ($\Delta_f H^\theta{}_m(cr)$) in $kJ \cdot mol^{-1}$ of mercury(II) chloride,[14] of the ligand,[15,17] of the ammonium chloride,[16,18] and eq 1. The results are given in Table 4, while the auxiliary data are listed in Table 5.

Table 3. Standard Molar Enthalpies of Solution-Reaction at 298 K

compound	solvent	solution	$\Delta_iH^\theta{}_m$ $kJ \cdot mol^{-1}$
$HgCl_{2(cr)}$	1,2-dichloroethane	A_1	3.66 ± 0.11
$2Me_2NH_2S_2CNMe_{2(cr)}$	A_1	A_2	−37.86 ± 2.50
$Hg(S_2CNMe_2)_{2(cr)}$	1,2-dichloroethane	A_3	29.16 ± 1.61
$2Me_2NH_2Cl_{(cr)}$	A_3	A_4	6.95 ± 0.22
$HgCl_{2(cr)}$	1,2-dichloroethane	B_1	3.66 ± 0.11
$2Pr^i{}_2NH_2S_2CNPr^i{}_{2(cr)}$	B_1	B_2	−45.89 ± 2.08
$Hg(S_2CNPr^i{}_2)_{2(cr)}$	1,2-dichloroethane	B_3	24.90 ± 2.17
$2Pr^i{}_2NH_2Cl_{(cr)}$	B_3	B_4	24.63 ± 0.37

Table 4. Standard Molar Enthalpies for the Complexes ($kJ \cdot mol^{-1}$)

parameter	$Hg(S_2CNMe_2)_2$	$Hg(S_2CNPr^i{}_2)_2$
$\Delta_rH^\theta{}_m$	−70.31 ± 2.98	−91.76 ± 3.03
$\Delta_fH^\theta{}_m(cr)$	−26.56 ± 7.89	−313.72 ± 3.31
$\Delta^g_{cr}H^\theta{}_m$	189.80 ± 0.91	187.70 ± 1.00
$\Delta_fH^\theta{}_m(g)$	163.24 ± 7.94	−126.02 ± 3.46
$\Delta_{ho}H^\theta{}_m$	−360.66 ± 9.10	−485.52 ± 5.56
$\Delta_{he}H^\theta{}_m$	−2824.47 ± 9.10	−2913.67 ± 6.57
$<D>(Hg-S)$	90.17 ± 9.10	121.38 ± 5.56
$<D'>(Hg-S)$	706.14 ± 9.10	728.42 ± 6.57

For the calculation of the enthalpies of dissociation of Hg−S bonds ($<D>$ and $<D'>$) in $kJ \cdot mol^{-1}$ as the complexes decomposed in the solid state, their enthalpies of sublimation are considered as being equal to the standard molar enthalpies of sublimation of the ligands.[19] Also, it is considered that the standard molar enthalpy of ligand decomposition is equal to its apparent enthalpy of sublimation.[7,8] The values found in the literature are: [(189.8 ± 0.9) and (187.7 ± 1.0)] $kJ \cdot mol^{-1}$, respectively.

The standard molar enthalpies of chelate formation in the gaseous phase, $\Delta_fH^\theta{}_m(g)$ in $kJ \cdot mol^{-1}$, and the mean energy of dissociation, $<D>$ and $<D'>$ in $kJ \cdot mol^{-1}$ of the Hg−S bonds were calculated according to hemolytic and heterolytic parameters. For these calculations, the values of the enthalpies of formation $\Delta_fH^\theta{}_m(^\bullet S_2CNR_{2(g)})$ and $\Delta_fH^\theta{}_m(^- S_2CNR_{2(g)})$ were estimated from experimental data of the enthalpies of formation of $\Delta_fH^\theta{}_m(HS_2CNR_2(g))$. According to the standard enthalpies of dissociation of S−H bonds in several compounds, Benson[20] determined that the dissociation enthalpy of the S−H bond is: $\Delta_mH^\theta(S-H) = (385.0 \pm 5.0)\ kJ \cdot mol^{-1}$.

The enthalpies of formation of radicals and anions[6,8] in the gaseous phase have been calculated by using the equations:

$$\Delta_fH^\theta{}_m(^\bullet S_2CNR_{2(g)}) = \Delta_mH^\theta(S-H) + \Delta_fH^\theta{}_m(HS_2CNR_{2(g)}) - \Delta_fH^\theta{}_m(^\bullet H_{(g)}) \qquad (2)$$

$$\Delta_fH^\theta{}_m(^- S_2CNR_{2(g)}) = E_L + \Delta_fH^\theta{}_m(^\bullet S_2CNR_{2(g)}) + \Delta_fH^\theta{}_m(e^-) \qquad (3)$$

The values of the enthalpies of formation of the complexes and the mean energies of dissociation of the Hg−S bonds using

Table 5. Auxiliary Data

species	$\Delta_f H^{\theta}{}_m$ kJ·mol^{-1}	ref
$HgCl_2$(cr)	−224.30 ± 0.30	14
$Me_2NH_2S_2CNMe_2$(cr)	−144.00 ± 6.40	15
Me_2NH_2Cl(cr)	−278.00 ± 3.52	16
$Pr^i{}_2NH_2S_2CNPr^i{}_2$(cr)	−349.60 ± 1.30	17
$Pr^i{}_2NH_2Cl$(cr)	−350.77 ± 0.15	18
Hg(g)	61.30 ± 0.01	14
Hg^{2+}(g)	2890.47 ± 0.03	14
$Me_2NCS^{\bullet}{}_2$(g)	231.30 ± 4.45	15
$Me_2NCS^{-}{}_2$(g)	−30.76 ± 4.45	8
$Pr^i{}_2NCS^{\bullet}{}_2$(g)	149.10 ± 4.35	17
$Pr^i{}_2NCS^{-}{}_2$(g)	−51.41 ± 4.35	17

hemolytic and heterolytic parameters are presented in Table 4. Auxiliary data that makes possible the calculations of $<D>$ (M−S) = $\Delta_{ho}H^{\theta}{}_m/4$ and $<D'>$ (M−S) = $\Delta_{he}H^{\theta}{}_m/4$ are presented in Table 5.

According to the literature, the stability of this kind of complex increases with the increase of the linear carbon chain. The stability decreases when alkyl substitution on the carbon chain is present. The results in Table 4 show, according to either $<D>$ or $<D'>$, that the isopropyl complex is more stable than the methyl complex. This behavior demonstrates clearly that, in the case of alkyl substitution, possible polar or steric effects did not affect directly the interaction Hg−S, as the final result did not indicate any dependence on either of these effects.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Schematic representation of $Hg[S_2CN(CH_3)_2]_2$.This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: 55(019)35213088. Fax: 55(019)35213023. E-mail: dunstan@iqm.unicamp.br.

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Notes

$^{\perp}$In memoriam.

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