Metal–sulphur bond enthalpy determination of diethyldithiocarbamate complexes of cadmium and mercury

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Abstract

The standard molar enthalpy of formation of crystalline diethyldithiocarbamate complexes of Cd and Hg(II) has been derived by solution calorimetry at 298.15 K, giving -227.5 ± 5.0 and -141.4 ± 5.0 kJ mol^{-1}, respectively. The corresponding standard molar enthalpies of sublimation, 102.0 ± 3.5 and 129.2 ± 4.2 kJ mol^{-1}, were estimated by means of differential scanning calorimetry. From the standard molar enthalpies of formation of the gaseous chelates (-125.5 ± 6.1 and -12.2 ± 6.5 kJ mol^{-1}), the homolytic (167.3 ± 3.6 and 74.6 ± 3.6 kJ mol^{-1}) and heterolytic (695.0 ± 3.6 and 733.4 ± 3.6 kJ mol^{-1}) mean metal–sulphur bond-dissociation enthalpies were calculated. The results correlate with the characteristics of the metals and cations in the gas phase.

INTRODUCTION

Despite the large number of publications concerned with the structural features of these compounds, the first thermochemical results appeared only at the end of the 1960s [1] and the first review including thermal data and solution thermochemistry of metal dithiocarbamate complexes and related compounds was published at the beginning of the 1980s [2, 3], followed by another recent review [4].

The enthalpies of formation of chelates of di-*n*-propyl, di-*n*-butyl and di-isobutyldithiocarbamates of Zn(II), Cd(II) and Hg(II) in the solid state have been obtained by solution–reaction calorimetry. From the thermochemical properties of these chelates in the gaseous phase, the enthalpies of the metal–sulphur bonds have been derived [5–7].

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This publication focuses on the thermochemical data for chelates of diethyldithiocarbamate with a complete series of zinc-group elements. These results are compared with those for di-*n*-propyl [5], di-*n*-butyl [6] and di-isobutyldithiocarbamates [7] of Zn(II), Cd(II) and Hg(II) and the di-ethyldithiocarbamate of Zn(II) [8] in order to help understand the effect of the length of the alkyl chain attached to the nitrogen of the ligand.

EXPERIMENTAL

Chemicals

Cadmium(II) and mercury(II) chlorides (Merck) were purified and dried in vacuo. Diethylamine and carbon disulphide were purified and distilled at 328 and 319 K, respectively. The solvents used in all preparations were distilled and kept dry. A solution of 5% HCl/CH$_3$OH was chosen as the calorimetric solvent because of its ability to dissolve diethylammonium chloride, metallic chlorides, ligands and chelates.

Preparations

All operations involved in the preparations and purifications were carried out either in vacuo or in a dry-box in an atmosphere of dried nitrogen for air-sensitive compounds [5–8].

The salts diethylammonium chloride and diethylammonium diethyl-dithiocarbamate were synthesized. Their analyses and melting points were in complete agreement with their formulation and reported melting points [7, 9].

The bis(diethyldithiocarbamate)s of cadmium and mercury were prepared by slowly adding a solution of diethylammonium diethyldithiocarbamate in ethanol to a stirred solution of the metal chloride in ethanol in 1:2 molar proportions [10]. White and yellow crystals of the cadmium and mercury chelates, respectively, were isolated, recrystallized from ethanol and dried in vacuo, with yields in the range 70–75%. Microanalyses for metal, carbon, hydrogen and nitrogen were within the experimental error of the expected values from the established formulae.

Calorimetric measurements

An LKB 8700-1 isoperibolic precision calorimeter system with a strip-chart recorder was used for all solution–reaction measurements. Details of the operational procedure, calculation method and the accuracy of the instrument are as described previously [5, 11]. The air-sensitive compounds were handled in dried nitrogen to prepare the ampoules. The enthalpies of fusion and the heat capacities of the solid and liquid forms of the chelates

TABLE 1

Mass percentage analyses (calculated values in parentheses) and C–N and C–S stretching wavenumbers (cm^{-1})

Compound	Analyses/%				IR Bands	
	M	C	H	N	v(C–N)	v(C–S)
$[Cd(S_2CNEt_2)_2]$	27.3 (27.5)	41.7 (41.5)	6.6 (6.9)	5.4 (5.4)	1483	984
$[Hg(S_2CNEt_2)_2]$	40.3 (40.4)	35.3 (35.4)	5.4 (5.9)	4.7 (4.6)	1482	985
$[NH_2Et_2S_2CNEt_2]$		61.2 (61.0)	11.1 (11.4)	8.3 (8.3)	1465	986
$[NH_2Et_2]Cl^a$				8.4 (8.4)		

[a] Cl 21.0 (21.3)%.

were determined in a Perkin-Elmer model DSC-7 differential scanning calorimeter purged with dry nitrogen [12]. For each determination the uncertainty interval is quoted as twice the standard deviation of the mean.

Other measurements

The melting temperatures for all compounds were determined by means of a Quimis model 340 apparatus. Thermogravimetric curves were obtained using a Perkin-Elmer model TGA-7 thermobalance at a heating rate of 10°C min^{-1} in a dry nitrogen stream in the temperature range 445–695 K. Infrared spectra were recorded for KBr pellets on a Perkin-Elmer model 467 spectrophotometer, and the mass spectra of the ligand and chelates were obtained on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV ($\approx 1.12 \times 10^{-17}$ J).

RESULTS AND DISCUSSION

The chelates of Cd and Hg showed narrow melting ranges of 521–522 and 390–391 K, respectively, and are in good agreement with those reported [13]. The mode of co-ordination of the dialkyldithiocarbamate and the small intervals of melting suggest the existence of very stable compounds. However, on cooling the melting sample and heating again, the previous melting point interval was not reproduced. Microanalytical data for ligand, chloride and chelates are listed in Table 1

The main infrared bands associated with the NCS$_2$ moiety of the ligand are also listed in Table 1. The CN band assumes double-bond character, which is reflected in the appearance of a stretching band shifted to higher frequency. For all complexes this band frequency is higher than that of the respective ligand. On the other hand, a decrease in the CS stretching band is observed and an isolated band near 1000 cm^{-1} indicates that the ligand is bonded in a bidentate manner to the metal [14–17].
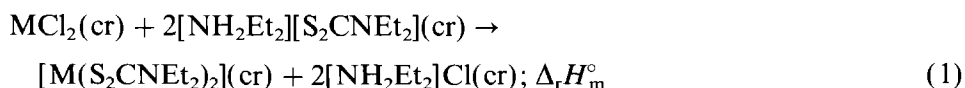
TABLE 2

Standard molar enthalpies (kJ mol^{-1}) of solution and reaction at 298.15 K

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m^\circ$
1	$2[NH_2Et_2][S_2CNEt_2](cr)$	5%HCl/CH$_3$OH	A$_1$	5	51.37 ± 0.27
2	$CdCl_2(cr)4$	A$_1$	A$_2$	5	60.31 ± 0.24
3	$2[NH_2Et_2]Cl(cr)$	5%HCl/CH$_3$OH	A$_3$	5	30.11 ± 0.46
4	$[Cd(S_2CNEt_2)_2](cr)$	A$_3$	A$_2$	5	18.06 ± 0.10
5	$HgCl_2(cr)$	5%HCl/CH$_3$OH	B$_1$	5	6.77 ± 0.14
6	$2[NH_2Et_2][S_2CNEt_2](cr)$	B$_1$	B$_2$	5	-59.84 ± 0.19
7	$2[NH_2Et_2]Cl(cr)$	5%HCl/CH$_3$OH	B$_3$	5	35.57 ± 0.23
8	$[Hg(S_2CNEt_2)_2](cr)$	B$_3$	B$_2$	5	49.57 ± 0.40

The mass spectra of dialkyldithiocarbamate complexes revealed the presence of the parent ions [18], which were observed for the diethyldithiocarbamate complexes with intensities of 28 and 2% for cadmium and mercury, respectively. In this work on diethyldithiocarbamate compounds of cadmium and mercury, the parent ions with corresponding intensities of 32.1 and 2.6% were obtained. The metal cations (M) appeared in two other peaks for all chelates: SMS_2CNEt_2 and MS_2CNEt_2. The other peaks were derived from ligand fragmentation, i.e. m/z 148 (S_2CNEt_2), 116 ($SCNEt_2$), 88 ($SCHNEt$), 76 (S_2C), 72 (Et_2N), 60 ($SCNH_2$) and 43 (Et).

The thermogravimetric results showed loss of mass before the melting temperature for the cadmium chelate and after this temperature for the mercury chelate. The thermogravimetric curve of the ligand shows loss of all mass in only one stage. The cadmium complex shows loss of the ligands plus a percentage of cadmium [$2(S_2CNEt_2) + \frac{1}{2}Cd$], which corresponds to 89.1% in the range 499–602 K, leaving a stable residue of 10.9% of the corresponding metal up to 602 K. For the mercury compound the weight loss occurred in two distinct steps of decomposition. In the first step (53.35%), $2(S_2CNEt_2)$ was eliminated in the range 445–551 K, followed by partial volatilization of the mercury (33.8%) in the range 633–695 K, leaving a residue of 8.2% up to 695 K.

The standard molar enthalpy of reaction $\Delta_r H_m^\circ$ was obtained at 298.15 K from the reaction–solution enthalpies $\Delta_i H_m^\circ$ of each reagent and product dissolved sequentially in a solution of 5% HCl/CH$_3$OH as calorimetric solvent (Table 2) for the following reaction [5–7]:

$$MCl_2(cr) + 2[NH_2Et_2][S_2CNEt_2](cr) \rightarrow$$

$$[M(S_2CNEt_2)_2](cr) + 2[NH_2Et_2]Cl(cr); \Delta_r H_m^\circ \tag{1}$$

The $\Delta_r H_m^\circ$ values were derived from these tabulated values by applying a convenient thermochemical cycle, and relevant data are listed in Table 3.

TABLE 3

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

	$Cd(S_2CNEt_2)_2$	$Hg(S_2CNEt_2)_2$
$\Delta_r H_m^\circ$	-57.11 ± 0.59	-138.21 ± 0.52
$\Delta_f H_m^\circ(cr)$	-227.5 ± 5.0	-141.4 ± 5.0
$\Delta_{cr}^l H_m^\circ$	24.2 ± 1.9	26.9 ± 2.1
$\Delta_{cr}^g H_m^\circ$	93.2 ± 1.3	97.6 ± 2.1
T_{fus}	522	387
T_{vap}	548	483
C_p, m(cr)	0.42 ± 0.01	0.32 ± 0.01
C_p, m(l)	0.50 ± 0.01	0.60 ± 0.01
C_p, m(g)	0.49 ± 0.01	0.44 ± 0.01
$\Delta_{cr}^g H_m^\circ$	102.0 ± 3.5	129.2 ± 4.2
$\Delta_f H_m^\circ(g)$	-125.5 ± 6.1	-12.2 ± 6.5
$\Delta_{ho} H_m^\circ$	-669.3 ± 14.3	-298.4 ± 14.6
$\Delta_{he} H_m^\circ$	-2780.0 ± 14.5	-2933.7 ± 14.5
$\langle D \rangle(M-S)$	167.3 ± 3.6	74.6 ± 3.6
$\langle D' \rangle(M-S)$	695.0 ± 3.6	733.4 ± 3.6

The standard molar enthalpies of formation of the crystalline chelates (Table 3) were determined from $\Delta_r H_m^\circ$ and the standard molar enthalpies of formation of the metal chlorides [19], ligand [20] and ammonium chloride [8] using expression (2), for which data are listed in Table 4.

$$\Delta_f H_m^\circ[M(S_2CNEt_2)_2](cr)$$

$$= \Delta_r H_m^\circ - 2\Delta_f H_m^\circ[NH_2Et_2]Cl(cr)$$

$$+ \Delta_f H_m^\circ[MCl_2](cr) + 2\Delta_f H_m^\circ[NH_2Et_2][S_2CNEt_2](cr) \qquad (2)$$

TABLE 4

Auxiliary data (kJ mol^{-1})

| Compound	$\Delta_f H_m^\circ$	Ref.
$CdCl_2(cr)$	-391.50 ± 0.22	19
$HgCl_2(cr)$	-224.30 ± 0.13	19
$[NH_2Et_2][S_2CNEt_2](cr)$	-249.2 ± 2.2	20
$[NH_2Et_2]Cl(cr)$	-359.73 ± 1.22	8
$Cd(g)$	112.01 ± 0.01	19
$Hg(g)$	61.30 ± 0.01	19
$S_2CNEt_2(g)$	2623.54 ± 0.02	19
$Cd^{2+}(g)$	2890.47 ± 0.03	19
$Hg^{2+}(g)$	215.9 ± 6.5	8
$-S_2CNEt_2(g)$	15.5 ± 6.5	12

To determine the metal–sulphur bond enthalpy for these chelates, it is indispensable to have information about the complexes in the gas phase. All attempts to measure directly the thermochemical parameters for the compounds in the gaseous phase were unsuccessful, owing to the difficulty of subliming the chelates. For this purpose the standard molar enthalpies of sublimation $\Delta_{cr}^{g}H_m^{\circ}$ were determined by means of differential scanning calorimetry (DSC) and estimation methods [5, 6, 12, 21, 22]. The molar standard enthalpies of fusion $\Delta_{cr}^{l}H_m^{\circ}$ were obtained from the sharp peaks at 522 and 387 K for the cadmium and mercury chelates respectively (Table 3). In these thermograms, the peaks due to vaporization at 548 and 483 K for the same sequence of complexes were used to estimate the enthalpies by the methods of Giacolone [23], Riedel–Planck–Miller [23] and Watson [24]. Table 3 lists the mean values obtained for the three estimation methods. The heat capacities for the solid and liquid phases, respectively, in the temperature ranges 463–473 and 532–542 K for the cadmium and 343–353 and 414–424 K for the mercury complexes were determined. However, for the gas phase these quantities were estimated [24] by means of eqn. (3):

$$C_{p}, m(g) = -0.0292 + 1.2553 \times 10^{-3}T - 0.5856 \times 10^{-6}T^2 \text{ (kJ mol}^{-1}) \quad (3)$$

The values obtained are listed in Table 3, together with the standard molar enthalpies of sublimation, which were calculated by applying all these auxiliary data in expression (4) and, consequently, the standard molar enthalpies of formation in the gas phase, listed in Table 3, were calculated

$$\Delta_{cr}^{g}H_m^{\circ} = \int_{298\,K}^{T_{fus}} C_p(s)\,dT + \Lambda_{cr}^{l}H_m^{\circ} + \int_{T_{fus}}^{T_{vap}} C_p(l)\,dT + \Lambda_{l}^{g}H_m^{\circ} + \int_{T_{vap}}^{298\,K} C_p(g)\,dT$$

$$(4)$$

Assuming that the metal is co-ordinated in a bidentate manner by each ligand, the mean bond-dissociation enthalpies of the chelates are related to one quarter of the standard molar enthalpy of disruption in homolytic, $\Delta_{ho}H_m^{\circ}$, or heterolytic, $\Delta_{he}H_m^{\circ}$, reactions [5, 6, 12, 21, 22]; see eqns. (5) and (6), respectively.

$$M(g) + 2 \cdot S_2CNEt_2(g) \rightarrow [M(S_2CNEt_2)_2](g); \Delta_{ho}H_m^{\circ} \quad (5)$$
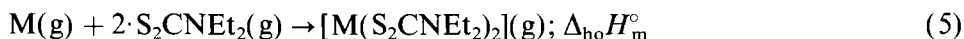
where

$$\Delta_{ho}H_m^{\circ} = \Delta_f H_m^{\circ}[M(S_2CNEt_2)_2](g) - \Delta_f H_m^{\circ}[M,g] - 2\Delta_f H_m^{\circ}[\cdot S_2CNEt_2](g)$$

$$M^{2+}(g) + 2^-S_2CNEt_2(g) \rightarrow [M(S_2CNEt_2)_2](g); \Delta_{he}H_m^{\circ} \quad (6)$$

where

$$\Delta_{he}H_m^{\circ} = \Delta_f H_m^{\circ}[M(S_2CNEt_2)_2](g) - \Delta_f H_m^{\circ}[M^{2+},g] - 2\Delta_f H_m^{\circ}[^-S_2CNEt_2](g)$$

From the auxiliary data listed in Table 4, one can calculate the mean enthalpy of the metal–sulphur bond for homolytic, $\langle D \rangle(M-S) =$

TABLE 5

Metal–sulphur bond-dissociation enthalpies for dialkyldithiocarbamates

Chelate	$\langle D \rangle (M-S)$	$\langle D' \rangle (M-S)$	Ref.
$Zn(S_2CNEt_2)_2$	177.4 ± 3.4	740.2 ± 3.5	8
$Zn(S_2CNPr_2^n)_2$	182 ± 3	745 ± 3	5
$Cd(S_2CNPr_2^n)_2$	154 ± 3	681 ± 3	5
$Hg(S_2CNPr_2^n)_2$	102 ± 3	709 ± 3	5
$Zn(S_2CNBu_2^n)_2$	183 ± 3	746 ± 3	5
$Cd(S_2CNBu_2^n)_2$	168 ± 3	694 ± 3	6
$Hg(S_2CNBu_2^n)_2$	105 ± 3	712 ± 3	6
$Zn(S_2CNBu_2^i)_2$	137 ± 4	700 ± 4	7
$Cd(S_2CNBu_2^i)_2$	118 ± 4	646 ± 4	7
$Hg(S_2CNBu_2^i)_2$	75 ± 4	682 ± 4	7

$-\Delta_{ho}H_m^\circ/4$ and for heterolytic, $\langle D' \rangle (M-S) = -\Delta_{he}H_m^\circ/4$ cleavage. In these determinations, the reorganization energy associated with the ligand upon complexation is neglected and an equivalence of all metal–sulphur bonds is assumed, even though for these complexes the metallic atoms are expected to be anisobidentately bonded by the sulphur atoms [15, 25].

The homolytic and heterolytic mean metal–sulphur bond enthalpies presented in Tables 3 and 5 show that $\langle D \rangle (M-S)$ decreases from zinc to mercury whereas $\langle D' \rangle (M-S)$ remains almost constant, as observed before with chelates of di-*n*-propyl [5], di-*n*-butyl [6] and di-isobutyldithiocarbamates [7].

In the absence of structural parameters, it is not possible to confirm the correlation between $\langle D \rangle (M-S)$ and the metal–sulphur bond distance, as was observed for any dialkyldithiocarbamate chelates of the phosphorus group which also showed a decrease in the mean element–sulphur bond enthalpy on going from phosphorus to bismuth [12, 21, 22].

The results presented in Tables 3 and 5 show that the values for $\langle D \rangle (M-S)$ and $\langle D' \rangle (M-S)$ follow the same sequence as the enthalpies of formation in the gas phase of the metals and cations, Table 4. This behaviour demonstrates clearly that, in the case of alkyl substituents, the polar effect and the steric effect are independent phenomena and the results do not indicate any clear dependence on either (or on a sum of the two). Moreover, both would presumably operate in the same direction in homolytic cleavage. Thus, these results appear to correlate better with the character of the metal, which is reflected in the homolytic and heterolytic bond enthalpy parameters, than with that of the ligand chain bonded to the coordination sites.

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