Thermochemical Features of Di-*n*-propyldithiocarbamate Chelates of Zinc-group Elements

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Solution-reaction calorimetry was used to determine the standard molar enthalpy of formation at 298.15 K of crystalline $[M(S_2CNPr^n_2)_2]$ (M = Zn, Cd or Hg): −440.68 ± 2.85, −396.71 ± 2.60 and −240.50 ± 2.40 kJ mol^{-1}, respectively. The enthalpies of sublimation, 147 ± 2, 199 ± 1 and 200 ± 2 kJ mol^{-1}, were estimated by means of differential scanning calorimetry. From the standard molar enthalpies of formation of the gaseous chelates, −294 ± 4, −198 ± 3 and −41 ± 3 kJ mol^{-1}, the homolytic 182 ± 3, 154 ± 3 and 102 ± 3 kJ mol^{-1} and heterolytic 745 ± 3, 681 ± 3 and 709 ± 3 kJ mol^{-1} mean metal-sulfur bond enthalpies were calculated. The homolytic enthalpies decrease from zinc to mercury and are dependent on the nature of the radical attached to the nitrogen of the ligand.

Dithiocarbamic acids are not easily isolated due to decomposition during the preparative process.[1] However, in solution the anionic species react strongly with a large number of metal cations to produce complexes, in which, with rare exceptions, the metals are co-ordinated by both sulfur atoms of the ligand. To avoid any problem with the dithiocarbamic acid synthesis, the anion form is normally isolated as a salt, by treating carbon disulfide with aliphatic or aromatic primary or secondary amines to give compounds of the general formula $NH_2R_2^+$-$R_2NCS_2^-$.[2] The corresponding alkali-metal salts are also prepared in basic media following this procedure. These salts are commonly used in many complexation reactions with the desired metal chloride or nitrate salts.[3]

The main purpose of this field of investigation was initially directed to the structural features of the complexes[4–6] and their large-scale analytical applicability.[7] Nowadays, thermochemical interest in these complexes has progressively increased. An important review of the thermochemistry of dithiocarbamate complexes, including dithiocarbonates and dithiophosphates, detailed such thermal properties as fusion, volatility, kinetics and mechanism of thermal decomposition, reaction-solution calorimetry and metal–sulfur bond dissociation enthalpy.[8]

Reported thermochemical data for nickel,[9] copper[10] and zinc[11] dialkyldithiocarbamate complexes showed that the mean metal–sulfur bond enthalpy correlated very well with the mean metal–sulfur bond distance observed in the solid compounds. A similar correlation was obtained for phosphorus-group elements.[12–14] For a series of dialkyldithiocarbamate ligands with nickel and copper, the mean metal–sulfur bond enthalpy has a parallel behaviour for both cations.[15] However, each individual value was dependent on the alkyl group attached to the nitrogen of the ligand, decreasing from butyl to ethyl for both metals and for phosphorus-group elements.

This publication focuses on the thermochemical data involving chelates of di-*n*-propyldithiocarbamate with a complete series of zinc-group elements. These results are compared with those for di-*n*-butyldithiocarbamate compounds[16] in order to help understand the effect of the length of the alkyl chain attached to the nitrogen of the ligand.

Experimental

Chemicals.—The solvents used in all preparations were distilled and kept dry. Divalent zinc, cadmium and mercury chlorides (Merck) were purified and dried *in vacuo*. Di-*n*-propylamine and carbon disulfide were purified and distilled at 383 and 319 K respectively. Acetone was used for all calorimetric measurements due to its ability to dissolve chlorides, salts and chelates.

Preparations.—Di-*n*-propylammonium chloride was prepared under anhydrous conditions by bubbling a stream of hydrogen chloride into a solution of the parent amine in acetone. The white crystals isolated were kept under dry nitrogen.[17]

Di-*n*-propylammonium di-*n*-propyldithiocarbamate was obtained from the reaction between an excess of carbon disulfide and the amine in acetone solution cooled in an ice–salt bath.[2] The filtered yellow crystals were recrystallized in acetone, dried *in vacuo* and stored as before.

Bis(di-*n*-propyldithiocarbamates) of zinc, cadmium and mercury were prepared by slowly adding an ethanolic solution of di-*n*-propylammonium di-*n*-propyldithiocarbamate to a stirred solution of the metal chloride in ethanol in 1:2 molar proportions, under anhydrous conditions.[18] White (zinc and cadmium) and yellow (mercury) crystals were isolated, recrystallized from ethanol and dried *in vacuo*, with yields in the range 75–85%. Microanalyses for metal, carbon, hydrogen and nitrogen were within experimental error of the expected values from the established empirical formulae.

Calorimetry.—The reaction-solution calorimetric measurements were performed in a LKB 8700-1 isoperibolic precision calorimetric system, as previously described.[16] Ampoules containing 10–60 mg of substrate were prepared in a dry-box and broken into a glass reaction vessel, charged with 0.10 dm^3 of a suitable calorimetric solvent at 298.15 ± 0.02 K.

The enthalpy of fusion and heat capacities of the chelates in solid or liquid forms were obtained in a DuPont model 910 differential scanning calorimeter, purged with dry nitrogen, coupled to the thermoanalyser and a programmed heat flow.[16]

Other Physical Measurements.—The melting points of the compounds were measured by a Quimis apparatus. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 467 spectrophotometer, mass spectra of the ligand and chelates on a Hewlett-Packard 5988 A spectrometer. Thermogravimetric

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

	Analysis						
Compound	M	C	H	N	T	ν(C–N)	ν(C–S)
$[NH_2Pr^n{}_2]Cl$*				10.2 (10.0)	543–545		
$[NH_2Pr^n{}_2][S_2CNPr^n{}_2]$		56.1 (56.0)	10.9 (10.7)	10.1 (10.0)	397–399	1458	980
$[Zn(S_2CNPr^n{}_2)_2]$	15.6 (15.5)	40.3 (40.4)	6.7 (6.5)	6.7 (6.5)	389–391	1485	971
$[Cd(S_2CNPr^n{}_2)_2]$	24.2 (24.0)	36.2 (37.0)	6.1 (6.1)	6.0 (5.8)	433–443	1490	972
$[Hg(S_2CNPr^n{}_2)_2]$	36.2 (36.2)	30.4 (30.6)	5.1 (4.9)	5.1 (4.9)	381–383	1480	964

* Cl 25.7 (25.3)%.

Table 2 Standard molar enthalpies (kJ mol^{-1}) of solution and reaction at 298.15 K (number of experiments in each case: 5)

Reactant	Solvent	Solution	$\Delta_i H^\circ_m$
$ZnCl_2$ (cr)	Acetone	A_1	-56.46 ± 0.43
$2[NH_2Pr^n{}_2][S_2CNPr^n{}_2]$ (cr)	A_1	A_2	19.64 ± 0.28
$[Zn(S_2CNPr^n{}_2)_2]$ (cr)	Acetone	A_3	42.12 ± 0.70
$2[NH_2Pr^n{}_2]Cl$ (cr)	A_3	A_2	19.29 ± 0.23
$2[NH_2Pr^n{}_2][S_2CNPr^n{}_2]$ (cr)	Acetone	B_1	34.51 ± 0.22
$CdCl_2$ (cr)	B_1	B_2	-56.45 ± 0.70
$2[NH_2Pr^n{}_2]Cl$ (cr)	Acetone	B_3	37.10 ± 0.09
$[Cd(S_2CNPr^n{}_2)_2]$ (cr)	B_3	B_2	18.77 ± 0.29
$HgCl_2$ (cr)	Acetone	C_1	6.30 ± 0.20
$2[NH_2Pr^n{}_2][S_2CNPr^n{}_2]$ (cr)	C_1	C_2	-35.82 ± 0.35
$[Hg(S_2CNPr^n{}_2)_2]$ (cr)	Acetone	C_3	44.71 ± 0.31
$2[NH_2Pr^n{}_2]Cl$ (cr)	C_3	C_2	14.57 ± 0.31

curves were obtained in a dynamic atmosphere of nitrogen, using a DuPont model 1090 thermobalance.

Results and Discussion

Microanalytical data for ligand, chloride and chelates are listed in Table 1. Sharp intervals of melting were observed for the chelates, in good agreement with those reported for zinc and cadmium.[2,17,19] The mercury compound was not previously isolated.

The positions of the CN and CS stretching bands shown in Table 1 elucidate the participation of the NCS_2 moiety of the ligand on co-ordination.[20] Thus, the CN bond assumes a double-bond character which is reflected in the appearance of a stretching band shifted to higher frequency. For all chelates this band is higher in frequency 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.[21–24]

The thermogravimetric curves[25] showed that the complexes decompose above the melting temperatures. The starting temperature of decomposition increases from 473, to 518 to 523 K, for zinc, cadmium and mercury chelates, respectively, reflecting the thermal stability. For the zinc compound a complete weight loss in only one stage in the range 473–618 K was observed. The cadmium chelate lost 85% of its weight in the range 518–628 K, which corresponds to $2S_2CNPr^n{}_2 + \frac{1}{2}Cd$, leaving a stable metal residue of 15% up to 628 K. Two stages were detected for the mercury chelate. In the first, 84% of the mass is lost in the range 523–628 K, corresponding to $2S_2CNPr^n{}_2 + \frac{1}{2}Hg$ fragments. The complement of this mass is lost in the range 628–763 K, due to volatilization of the remaining metal.

Mass spectra obtained with an ionization energy of 70 eV (*ca.* 1.12×10^{-17} J) are very similar for all chelates with the parent ion detected with intensities of 40, 19 and 4% for zinc, cadmium and mercury, respectively. This is the same stability order as that obtained by fragmentation with electron impact, as previously reported.[26] The cations (M) appeared in two other peaks for all chelates: $SMS_2CNPr^n{}_2$ and $MS_2CNPr^n{}_2$. The other peaks were derived from the ligand fragmentation, i.e. m/z 176 ($S_2CNPr^n{}_2$), 144 ($SCNPr^n{}_2$), 102 ($SCHNPr^n$), 101 ($SCNPr^n$), 76 (S_2C), 72 (SNC_2H_2), 70 ($HCNPr^n$), 60 ($SCNH_2$) and 43 (Pr^n).

The standard molar enthalpies of formation of $[M(S_2CNPr^n{}_2)_2]$ (M = Zn, Cd or Hg) were determined at 298.15 K by means of the general thermochemical reaction (1).[16] The

$$MCl_2\,(cr) + 2[NH_2Pr^n{}_2][S_2CNPr^n{}_2]\,(cr) \longrightarrow [M(S_2CNPr^n{}_2)_2]\,(cr) + 2[NH_2Pr^n{}_2]Cl\,(cr); \Delta_r H^\circ_m \quad (1)$$

standard molar enthalpy of this reaction was obtained by measuring the enthalpy of dissolution of each reactant and product successively in acetone as calorimetric solvent. The sequence of the various steps of dissolution is presented in Table 2. In each reaction a strict control of the stoichiometries was maintained so that the final solution of the reactants had the same composition as the products. The $\Delta_r H^\circ_m$ values were derived from these tabulated values by applying a convenient thermochemical cycle, relevant data being listed in Table 3.

The standard molar enthalpies of formation of the crystalline chelates (Table 3) were determined from $\Delta_r H^\circ_m$ and the standard molar enthalpies of formation of the metal chlorides,[27] ligand[28] and ammonium chloride.[29] The data are listed in Table 4.

Thermochemical data for these compounds in the gas phase are indispensable for the determination of the metal–sulfur bond enthalpy. However, all attempts to sublime them were unsuccessful. Therefore, the standard molar enthalpy of sublimation, $\Delta^g_{cr} H^\circ_m$, was determined by means of differential scanning calorimetry (DSC) and estimative methods.[16] For all complexes the DSC curves showed one sharp and one broad peak. The first peak was identified with fusion at 382 (Zn), 431 (Cd) and 372 K (Hg), from which the standard molar enthalpies of fusion, $\Delta^l_{cr} H^\circ_m$ were calculated (Table 3). From the second peak, at 593 (Zn), 571 (Cd) and 549 K (Hg), the temperature of vaporization and consequently the standard molar enthalpy of vaporization was estimated by means of Giacolone,[31] Riedel–Planck–Miller[31] and Watson methods.[32] The heat capacities for the solid chelates in the ranges 355–365 (Zn), 405–415 (Cd) and 354–364 K (Hg), and for the liquid phase in the ranges 395–405 (Zn), 451–461 (Cd) and 395–405 K (Hg) were determined. The heat capacities in the gas phase were estimated by the method of generalized vibrational assignment by means of the expression $C_p(g) = -0.056 + 1.612 \times 10^{-3}\,T - 0.729 \times 10^{-6}\,T^2$. All these quantities are listed in Table 3. From these data the standard enthalpies of sublimation were calculated for all chelates by applying the tabulated data (Table 3) in expression (2).

$$\Delta^g_{cr} H^\circ_m\,(298\ K) = \int_{298}^{T_{fus}} C_p(cr)\,dT + \Delta^l_{cr} H^\circ_m(T_{fus}) + \int_{T_{fus}}^{T_{vap}} C_p(l)\,dT + \Delta^g_l H^\circ_m(T_{vap}) - \int_{298}^{T_{vap}} C_p(g)\,dT \quad (2)$$

The standard molar enthalpies of formation of all chelates in

Table 3 Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ K^{-1} mol^{-1}), homolytic and heterolytic quantities (kJ mol^{-1})

	$[Zn(S_2CNPr^n{}_2)_2]$	$[Cd(S_2CNPr^n{}_2)_2]$	$[Hg(S_2CNPr^n{}_2)_2]$
$\Delta_r H^\circ_m$	-98.23 ± 0.90	-77.81 ± 0.79	-88.80 ± 0.59
$\Delta_f H^\circ_m$ (cr)	-440.68 ± 2.85	-396.71 ± 2.60	-240.50 ± 2.40
$\Delta^l_{cr} H^\circ_m$	30.35 ± 0.25	23.72 ± 0.19	33.37 ± 0.21
$\Delta^g_l H^\circ_m$	60.92 ± 1.51	61.53 ± 1.08	63.05 ± 1.74
$C_{p,m}$ (cr)	0.56 ± 0.10	0.66 ± 0.02	0.78 ± 0.02
$C_{p,m}$ (l)	0.81 ± 0.01	1.22 ± 0.01	0.99 ± 0.01
$C_{p,m}$ (g)	0.55 ± 0.14	0.53 ± 0.13	0.51 ± 0.12
$\Delta^g_{cr} H^\circ_m$	147 ± 2	199 ± 1	200 ± 2
$\Delta_f H^\circ_m$ (g)	-294 ± 4	-198 ± 3	-41 ± 3
$\Delta_{ho} H^\circ_m$	-728 ± 12	-614 ± 12	-406 ± 12
$\Delta_{he} H^\circ_m$	-2980 ± 12	-2724 ± 12	-2834 ± 12
$\langle D \rangle$(M–S)	182 ± 3	154 ± 3	102 ± 3
$\langle D' \rangle$(M–S)	745 ± 3	681 ± 3	709 ± 3

Table 4 Auxiliary data (kJ mol^{-1})

Substance	$\Delta_f H^\circ_m$	Ref.
$ZnCl_2$ (cr)	-415.05 ± 0.02	27
$CdCl_2$ (cr)	-391.50 ± 0.22	27
$HgCl_2$ (cr)	-224.30 ± 0.13	27
$[NH_2Pr^n{}_2][S_2CNPr^n{}_2]$ (cr)	-353.2 ± 1.3	28
$[NH_2Pr^n{}_2]Cl$	-389.5 ± 1.0	29
Zn (g)	130.73 ± 0.01	27
Cd (g)	112.01 ± 0.01	27
Hg (g)	61.32 ± 0.01	27
Zn^{2+} (g)	2782.78 ± 0.03	27
Cd^{2+} (g)	2623.54 ± 0.02	27
Hg^{2+} (g)	2890.47 ± 0.03	27
$Pr^n{}_2NCS_2H$ (g)	-15.2 ± 3.9	30
$Pr^n{}_2NCS_2{}^\bullet$ (g)	151.8 ± 5.6	*
$Pr^n{}_2NCS_2{}^-$ (g)	-48.6 ± 5.6	*

* This work (see text).

the gas phase were calculated and are listed in Table 3. Assuming that the metal is co-ordinated in a bidentate manner by each ligand, the mean bond-dissociation enthalpy of the complexes is related to one fourth of the standard molar enthalpy of disruption in a homolytic ($\Delta_{ho}H^\circ_m$) or heterolytic ($\Delta_{he}H^\circ_m$) reaction,[13,14,16] equations (3) and (4). For these

$$M(g) + 2{}^\bullet S_2CNPr^n{}_2(g) \longrightarrow [M(S_2CNPr^n{}_2)_2](g);\ \Delta_{ho}H^\circ_m \quad (3)$$

$$M^{2+}(g) + 2{}^-S_2CNPr^n{}_2(g) \longrightarrow [M(S_2CNPr^n{}_2)_2](g);\ \Delta_{he}H^\circ_m \quad (4)$$

determinations the standard molar enthalpy of formation of the metal[27] and the respective cation[27] are shown in Table 4. The standard enthalpy of formation of the ligand radical (151.8 ± 5.6 kJ mol^{-1}) and anion (-48.6 ± 5.6 kJ mol^{-1}), also included in Table 4, were derived from the standard molar enthalpy of formation of the acid in the gaseous phase[30] (-15.2 ± 3.9 kJ mol^{-1}), by considering the known auxiliary thermochemical quantities (Table 4): $D(S\text{–}H) = 385 \pm 4$,[15] $\Delta_f H^\circ_m(H,g) = 218.00 \pm 0.04$[11] and the electron affinity of the sulfur atom[11] -200.42 ± 0.05 kJ mol^{-1}.

The standard molar disruption enthalpies shown in Table 3 were obtained by neglecting the reorganization energy associated with the ligand upon complexation and supposing that all metal–sulfur bonds are equivalent, even though for these chelates the metal atoms are expected to be anisobidentately bonded by the sulfur atoms.[16]

The homolytic and heterolytic mean metal–sulfur bond enthalpies presented in Table 3 showed that $\langle D \rangle$(M–S) decreases from zinc to mercury while $\langle D' \rangle$(M–S) remains almost constant, as observed before with chelates of di-*n*-butyldithiocarbamate.[16] On the other hand the sparse mean metal–sulfur bond enthalpies for adducts of thioacetamide and thiobenzamide showed a slight increase from zinc to cadmium followed by a small drop to mercury.[33] However, for some phosphorus-group chelates similar correlations were obtained between the mean element–sulfur enthalpies and mean element–sulfur bond distance for known crystalline structures.[12,13]

Another feature to be examined is related to the thermochemical data for series of dialkyldithiocarbamates. Thus, the $\langle D \rangle$(M–S) values are 183 ± 3, 168 ± 3 and 105 ± 3 kJ mol^{-1} for zinc, cadmium and mercury di-*n*-butyldithiocarbamates,[16] somewhat higher than the corresponding values for the di-*n*-propyldithiocarbamates, as shown in Table 3. For dialkyldithiocarbamates of copper and nickel a similar trend with increase in $\langle D \rangle$(M–S) values when ethyl is substituted by other alkyl groups was interpreted as a mesomeric effect of the NR_2 groups.[15] In the present case, the higher values for the di-*n*-butyldithiocarbamates might be associated with the larger inductive effect of the Bu^n radicals, which overcomes any possible steric effect.[16] Other thermochemical determinations in progress may elucidate this. Nevertheless, the tendency is confirmed by $\langle D \rangle$(Zn–S) for diethyldithiocarbamate, which has the value of 170 ± 3 kJ mol^{-1}.[11]

Acknowledgements

The authors are indebted to CNPq for support. One of us, M. A. R. P. C., acknowledges CAPES for a fellowship.

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Received 18*th October* 1991; *Paper* 1/05301I