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Thermochemical parameters of complexes of di-*n*-propyldithiocarbamate of phosphorus-group elements

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Abstract

The standard molar enthalpy of formation of crystalline di-*n*-propyldithiocarbamate complexes of P, As, Sb and Bi(III) was determined through reaction–solution calorimetry in acetone, at 298.15 K, giving −661.10±5.04, −305.07±5.50, −366.62±1.70 and −358.98±1.70 kJ mol^{-1}, respectively. The corresponding standard molar enthalpies of sublimation were 127.36±4.24, 145.07±5.30, 169.45±6.08 and 185.24±5.03 kJ mol^{-1}, respectively, estimated by means of differential scanning calorimetry. By combining the preceding values with the standard molar enthalpies of formation of the chelates in the solid phase, the standard molar enthalpies of formation in the gas phase was obtained as −533.74±7.28, −160.00±6.10, 197.17±6.31 and 173.74±5.31 kJ mol^{-1}, respectively. From the standard molar enthalpies of formation of the gaseous chelates, the homolytic values were 217.3±3.1, 153.0±3.0, 152.5±3.0 and 139.5±2.9, and the heterolytic values were 1091.3±3.1, 969.2±3.0, 867.1±3.0 and 838.5±2.9 kJ mol^{-1}, and the mean metal–sulphur bond-dissociation enthalpies were calculated.

Keywords: Calorimetry; Di-*n*-propyldithiocarbamate; Phosphorus; Enthalpy; Bismuth

1. Introduction

In spite of the large number of publications concerned with the structural features of dithiocarbamate compounds, the first thermochemical results appeared only at the end of 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 eighties decade [2,3] followed by another recent review [4].

The enthalpies of formation of chelates of diethyl, di-*n*-butyl and di-iso-butyldithiocarbamate of P, As, Sb and Bi(III) 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. The decrease of the element–sulphur enthalpy from phosphorus to bismuth was interpreted as a reduced overlap of the d orbitals in bond formation [5–8].

This publication focuses on the thermochemical data for chelates of di-*n*-propyldithiocarbamate with P, As, Sb and Bi(III) elements. These results are

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compared with those for diethyl, di-*n*-butyl and di-isobutyldithiocarbamate compounds [5–8] in order to help understand the effect of the length of the alkyl chain attached to the nitrogen of the ligand.

2. Experimental

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.

2.1. Chemicals

The solvents used in all preparations were distilled and stored over Linde 4A molecular sieves. Di-*n*-propylamine (Merck) and carbon disulphide (Merck) were purified and distilled at 383 and 319 K, respectively. PCl_3 (Merck) and $AsCl_3$ (Carlo Erba) were carefully distilled before use. $SbCl_3$ (Merck) and $BiCl_3$ (Carlo Erba) were purified by sublimation in vacuo. Dried acetone was chosen as the calorimetric solvent due to its ability to dissolve the chlorides, ligand and chelates.

2.2. Preparations

The salts di-*n*-propylammonium chloride and di-*n*-propylammonium di-*n*-propyldithiocarbamate were synthesized. Their analysis and melting points were in complete agreement with their formulation and reported melting points [9,10].

The compounds $[E(S_2CNPr^n_2)_3]$ where (E=P, As, Sb and Bi) were prepared by slowly adding a solution of $[H_2NPr^n_2][S_2CNPr^n_2]$ in acetone to a stirred solution of the ECl_3 in acetone in 1:3 molar proportions [5–8]. After filtration, the crystals formed were washed with petroleum ether, which were recrystallized from acetone and dried in vacuo, with yields in the range 73–79%. The complexes obtained were stored in a desiccator over calcium chloride. Microanalysis for carbon, hydrogen and nitrogen were within experimental error of the expected values from the established formulas.

2.3. Physical measurements

The melting temperatures for all compounds were determined by means of a Microquímica model MQAPF-301 apparatus. Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance, at a heating rate of 0.083 K s^{-1} in a dry nitrogen flux of 3.33 $cm^3\,s^{-1}$. Infrared spectra were recorded as KBr pellets in the region 4000–400 cm^{-1} using a Bomem model MB-102 series FT-IR spectrophotometer, and the mass spectra of the ligand and chelates were recorded on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV at 523 K.

2.4. Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 isoperibolic precision calorimeter system as described before [5]. The solution calorimetric measurements were performed by dissolving samples of 15–25 mg of salts or chelates in 100 cm^3 of calorimetric solvent, maintaining a molar relation stoichiometry. The air-sensitive compounds were handled in dried nitrogen to prepare the ampoules. Uncertainty intervals are quoted as twice the standard deviations of the means of about seven replicate measurements on each compound. Combined errors were calculated from the square root on the sum of the square of the component errors.

The enthalpies of fusion, and the heat capacities of the solid and liquid forms of the chelates were determined in a Shimadzu model DSC-50 differential scanning calorimeter at a heating rate 0.083 K s^{-1} purged with dry nitrogen [11,12].

3. Results and discussion

The chelates $[E(S_2CNPr^n_2)_3]$ where (E=P, As, Sb and Bi) showed narrow melting intervals, 398–399, 396–397, 425–427 and 443–445 K, for the sequence of listed compounds. The characteristic mode of coordination of the dialkyldithiocarbamate anions 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 chelates were within experimental error of the expected values from the established formulae as listed in Table 1.

Table 1
Mass percentage analysis (calculated values in parentheses)

Compounds	C (%)	H (%)	N (%)	Cl (%)
$[P(S_2CNPr^n_2)_3]$	(45.04) 44.99	(7.57) 7.52	(7.50) 7.43	–
$[As(S_2CNPr^n_2)_3]$	(41.80) 41.02	(6.97) 6.93	(6.97) 6.87	–
$[Sb(S_2CNPr^n_2)_3]$	(38.78) 37.87	(6.46) 6.47	(6.46) 6.17	–
$[Bi(S_2CNPr^n_2)_3]$	(34.19) 34.17	(5.69) 5.60	(5.69) 5.64	–
$[Pr^n_2NH_2][S_2CNPr^n_2]$	(56.12) 56.02	(10.79) 10.20	(10.07) 9.46	–
$[Pr^n_2NH_2]Cl$	–	–	(10.18) 9.95	(25.08) 25.09

The mode of vibration related to CN stretching frequency band conformed to the fact that the bond assumes a double-bond character reflecting in the shift to higher frequency: 1476, 1490, 1481 and 1485 cm^{-1} for P, As, Sb and Bi, respectively. For all complexes, this band frequency is higher than that observed for the respective free ligand. On the other hand, the assigned CS stretching frequency band is observed in all spectra as an isolated band near 1000 cm^{-1}. This established behaviour indicates that the ligand is bonded in a bidentate manner to metal [13–15] as shown at 1008, 990, 975 and 970 cm^{-1} for P, As, Sb and Bi, respectively. The mass spectra of the complexes did not reveal the presence of the parent ions. The thermogravimetric curves showed loss of mass below the melting temperature for phosphorus and arsenic and above that of antimony and bismuth chelates.

The standard molar enthalpy of reaction, $\Delta_r H^0_m$, was obtained at 298.15 K from the reaction–solution enthalpies, $\Delta_i H^0_m$, of each reagent and product dissolved sequentially in acetone (Table 2), where a strict control of stoichiometry was maintained for the following general reaction [5,8,9,16]:

$$\begin{aligned} &ECl_3(l, cr) + 3NH_2Pr^n_2S_2CNPr^n_2(cr) \\ &\quad \rightarrow E(S_2CNPr^n_2)_3(cr) + 3NH_2Pr^n_2Cl(cr);\quad \Delta_r H^0_m \end{aligned}$$

The standard molar enthalpy for each reaction was performed from these tabulated values by applying a convenient thermochemical cycle, whose individual enthalpy values are listed in Table 3.

The standard molar enthalpies of formation of the crystalline chelates shown in Table 3 were determined from $\Delta_r H^0_m$, and the respective standard molar enthalpies of formation of the metal chlorides [17], ligand

Table 2
Standard molar enthalpies ($kJ\ mol^{-1}$) of solution–reaction at 298.15 K

Reactant	Solvent	Solution	No. of experiments	$\Delta_i H^0_m$
$3[Pr^n_2NH_2][S_2CNPr^n_2](cr)$	Acetone	A_1	6	54.41±0.16
$PCl_3(l)$	A_1	A_2	6	−328.13±1.04
$3[Pr^n_2NH_2]Cl(cr)$	Acetone	A_3	6	18.06±0.05
$[P(S_2CNPr^n_2)_3](cr)$	A_3	A_4	6	49.19±0.08
$AsCl_3(l)$	Acetone	B_1	6	−6.77±0.05
$3[Pr^n_2NH_2][S_2CNPr^n_2](cr)$	B_1	B_2	6	−46.19±0.28
$3[Pr^n_2NH_2]Cl(cr)$	Acetone	B_3	6	11.59±0.26
$[As(S_2CNPr^n_2)_3](cr)$	B_3	B_4	6	44.42±1.20
$SbCl_3(cr)$	Acetone	C_1	6	−23.03±0.10
$3[Pr^n_2NH_2][S_2CNPr^n_2](cr)$	C_1	C_2	6	−20.60±0.42
$3[Pr^n_2NH_2]Cl(cr)$	Acetone	C_3	6	11.65±0.05
$[Sb(S_2CNPr^n_2)_3](cr)$	C_3	C_4	6	38.07±0.15
$BiCl_3(cr)$	Acetone	D_1	6	−29.69±0.13
$3[Pr^n_2NH_2][S_2CNPr^n_2](cr)$	D_1	D_2	6	−19.47±0.36
$3[Pr^n_2NH_2]Cl(cr)$	Acetone	D_3	6	28.29±0.23
$[Bi(S_2CNPr^n_2)_3](cr)$	D_3	D_4	6	11.33±0.05

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

Parameters	$[P(S_2CNPr^n_2)_3]$	$[As(S_2CNPr^n_2)_3]$	$[Sb(S_2CNPr^n_2)_3]$	$[Bi(S_2CNPr^n_2)_3]$
$-\Delta_r H^0_m$	450.33±1.06	108.97±1.26	93.35±0.46	88.78±0.45
$-\Delta_f H^0_m(cr)$	661.1±5.04	305.07±5.50	366.62±4.94	358.98±4.24
$\Delta^l_{cr} H^0_m$	32.00±0.13	40.13±0.52	43.80±0.91	42.63±0.36
$\Delta^g_l H^0_m$	40.01±0.09	54.46±5.24	59.29±5.94	65.25±5.01
T_{fus}	398.1±0.6	395.0±0.37	423.2±0.4	441.1±0.2
T_{vap}	484.2±0.5	532.3±0.7	559.0±0.4	581.3±0.5
$C_{p,m}(cr)$	0.814±0.079	1.088±0.093	1.075±0.016	1.176±0.032
$C_{p,m}(l)$	0.971±0.081	1.127±0.028	1.281±0.021	1.278±0.051
$C_{p,m}(g)$	0.589±0.096	0.895±0.102	0.928±0.112	0.953±0.122
$\Delta^g_{cr} H^0_m$	127.36±5.25	145.07±5.30	169.45±6.08	185.24±5.03
$-\Delta_f H^0_m(g)$	533.74±7.28	160.00±6.10	197.17±6.31	173.74±5.31
$-\Delta_{ho} H^0_m$	1303.7±18.3	917.9±17.8	914.9±17.9	836.2±17.6
$-\Delta_{he} H^0_m$	6548.0±18.3	5815.3±17.9	5202.4±17.9	5031.0±17.7

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

Compound	$-\Delta_f H^0_m$	Ref.
$PCl_3(l)$	319.7±0.3	[17]
$AsCl_3(l)$	305.0±2.2	[17]
$SbCl_3(cr)$	382.17±0.06	[17]
$BiCl_3(cr)$	379.10±0.10	[17]
$[Pr^n_2NH_2][S_2CNPr^n_2](cr)$	353.20±1.30	[18]
$[Pr^n_2NH_2]Cl(cr)$	389.50±1.00	[19]
P(g)	−314.6±0.2	[17]
As(g)	−302.5±0.2	[17]
Sb(g)	−262.3±0.1	[17]
Bi(g)	−207.1±0.1	[17]
$P^{3+}(g)$	−6160.1±0.1	[17]
$As^{3+}(g)$	−5801.1±0.1	[17]
$Sb^{3+}(g)$	−5151.0±0.4	[17]
$Bi^{3+}(g)$	−5004.0±1.7	[17]
$Pr^n_2NCS_2(g)$	−151.8±5.6	[22]
$Pr^n_2NCS^-_2(g)$	−48.6±5.6	[9]

[18] and ammonium chloride [19] was obtained by using expression (2), where the auxiliary data are listed in Table 4.

$$\begin{aligned}\Delta_f H^0_m[E(S_2CNPr^n_2)_3](cr) &= \Delta_r H^0_m \\ &- 3\Delta_f H^0_m(NH_2Pr^n_2Cl)(cr) + \Delta_f H^0_m(ECl_3)(cr) \\ &+ 3\Delta_f H^0_m(NH_2Pr^n_2S_2CNPr^n_2)(cr). \qquad (2)\end{aligned}$$

The standard molar enthalpies of sublimation, $\Delta^g_{cr} H^0_m$, were determined by means of differential scanning calorimetry and estimative methods [5–8]. The molar standard enthalpies of vapourization were determined through these three estimative methods: Watson [20], Giacolone [21], and Riedel–Planck–Miller [21]. The molar standard enthalpies of fusion and heat capacities for the solid and liquid phases of the complexes were determined by means of DSC technique. However, for the heat capacities gas phase these quantities were estimated by Dobratz method [20]. A complete series of these values obtained are listed in Table 3, together with the standard molar enthalpies of sublimation. These values were calculated by applying all these auxiliary data in the expression (3) and consequently the standard molar enthalpies of formation in the gas phase, listed in Table 3, were calculated.

$$\begin{aligned}\Delta^g_{cr} H^0_m = &\int_{298.15\,\mathrm{K}}^{T_{fus}} C_p(cr)\,dT + \Delta^l_{cr} H^0_m \\ &+ \int_{T_{fus}}^{T_{vap}} C_p(l)\,dT + \Delta^g_l H^0_m \\ &+ \int_{T_{vap}}^{-298.15\,\mathrm{K}} C_p(g)\,dT. \qquad (3)\end{aligned}$$

The auxiliary data listed in Table 4 enables the calculation of the mean enthalpy of element–sulphur bond [5–9,11,12] for homolytic, $\langle D\rangle$(E–S)= $\Delta_{ho} H^0_m/6$, and for heterolytic, $\langle D'\rangle$(E–S)= $\Delta_{he} H^0_m/6$, whose values are listed in Table 5.

These homolytic mean enthalpy of element–sulphur bond, $\langle D\rangle$(E–S), values decreased from phosphorous

Table 5
Mean enthapies of the element–sulphur bond, homolitic, $\langle D\rangle$(E–S), and heterolitic, $\langle D'\rangle$(E–S), for dialkyldithiocarbamates

Chelates	$\langle D\rangle$(E–S)	$\langle D'\rangle$(E–S)	Ref.
$[\mathrm{P(S_2CNEt^{\mathit{n}}_2)_3}]$	187.3±3.5	1061.3±3.5	[5]
$[\mathrm{P(S_2CNPr^{\mathit{n}}_2)_3}]$	217.3±3.1	1091.3±3.1	a
$[\mathrm{P(S_2CNBu^{\mathit{n}}_2)_3}]$	214.2±3.5	1155.0±2.7	[7]
$[\mathrm{P(S_2CNBu^{\mathit{i}}_2)_3}]$	190.0±3.9	1064.2±3.9	[8]
$[\mathrm{As(S_2CNEt^{\mathit{n}}_2)_3}]$	155.1±3.5	971.8±3.5	[5]
$[\mathrm{As(S_2CNPr^{\mathit{n}}_2)_3}]$	153.0±3.0	969.2±3.0	a
$[\mathrm{As(S_2CNBu^{\mathit{n}}_2)_3}]$	169.7±3.4	1052.8±3.4	[7]
$[\mathrm{As(S_2CNBu^{\mathit{i}}_2)_3}]$	164.8±3.8	981.1±3.8	[8]
$[\mathrm{Sb(S_2CNEt^{\mathit{n}}_2)_3}]$	151.9±3.4	866.5±3.5	[6]
$[\mathrm{Sb(S_2CNPr^{\mathit{n}}_2)_3}]$	152.5±3.0	867.1±3.0	a
$[\mathrm{Sb(S_2CNBu^{\mathit{n}}_2)_3}]$	168.4±3.3	949.8±3.3	[7]
$[\mathrm{Sb(S_2CNBu^{\mathit{i}}_2)_3}]$	160.8±3.9	875.4±3.9	[8]
$[\mathrm{Bi(S_2CNEt^{\mathit{n}}_2)_3}]$	137.6±3.5	836.8±3.5	[6]
$[\mathrm{Bi(S_2CNPr^{\mathit{n}}_2)_3}]$	139.4±2.9	838.5±2.9	a
$[\mathrm{Bi(S_2CNBu^{\mathit{n}}_2)_3}]$	156.1±3.4	922.2±3.4	[7]
$[\mathrm{Bi(S_2CNBu^{\mathit{i}}_2)_3}]$	150.3±3.9	849.9±3.9	[8]

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to bismuth. Therefore, the larger $\langle D\rangle$(P–S) value was interpreted as a better overlap of d orbitals of P and S atoms in the bond formation. The less effective π bonding in the Bi–S bond is expected as a consequence of the increase of the hardness of the Bi atom, which can cause a decrease in $\langle D\rangle$(Bi–S) value. Similar behaviour was observed for chelates involving diethyl-, di-*n*-butyl- and di-isobutyldithiocarbamates for the same sequence of elements [5–8].

The results presented in Table 5 show that $\langle D\rangle$(E–S) and $\langle D'\rangle$(E–S) values follow the same sequence as those observed for the enthalpies of formation of the elements and cations in the gas phase, Table 4. A graphical representation is shown in Figs. 1 and 2. This behaviour demonstrates clearly that, in case of alkyl substituents, the possible polar or steric effect related to the ligands did not affect the phenomena and the final result did not indicate any clear dependence on either. However, these results appear to correlate better with the character of the element, which can be reflected on the homolytic and heterolytic bond enthalpy parameters, than with that of the ligand chain bonded to the coordination sites. Similar conclusion was observed before with dialkyldithiocarbamate chelates of zinc-group elements [22].

In the absence of structural parameters, it is not possible to confirm the correlation between homolytic mean enthalpy of element–sulphur bond and the mean element–sulphur bond distance, as was observed for diethyl- and di-*n*-butyldithiocarbamate complexes of the phosphorus group elements [7]. In that kind of correlation, it was observed as a decrease in these thermochemical data with the increase of the atomic number of these elements.

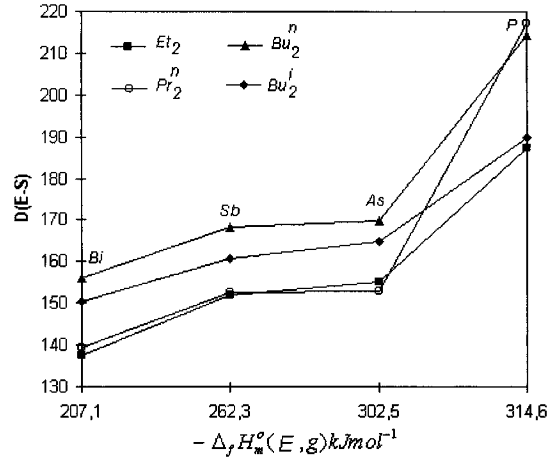

Fig. 1. Correlation between homolitic mean bond enthalpies, $\langle D\rangle$(E–S), and enthalpies of formation, $\Delta_f H^0_m$, of the elements in gas phase.

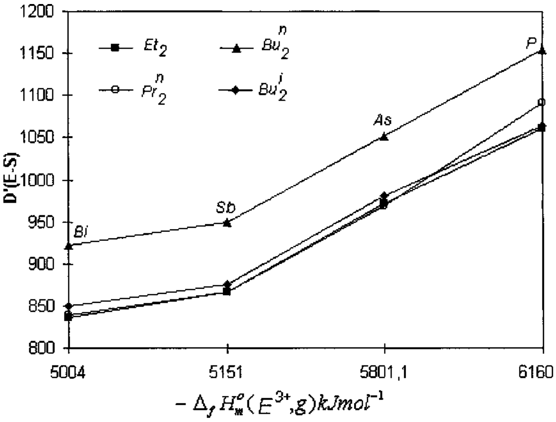

Fig. 2. Correlation between heterolitic mean bond enthalpies, $\langle D\rangle$(E–S), and enthalpies of formation, $-\Delta_f H^0_m$, of the cations in gas phase.

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