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Thermochemical parameters of dialkyldithiocarbamate chelates of indium(III)

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Abstract

A series of dialkyldithiocarbamate chelates of indium(III) of the general formula $In(S_2CNR_2)_3$, ($R = C_2H_5$, n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9), were prepared from the reaction of hydrochloric acid solution of metallic indium and the corresponding dialkylammonium salt of the ligand at pH = 3–4, giving yields better than 78%. The standard molar enthalpies of formation of crystalline dialkyldithiocarbamate chelates of In(III), were determined through reaction-solution calorimetry in acetone, at 298.15 K. The corresponding standard molar enthalpies of sublimation were estimated by means of differential scanning calorimetry. By combining of the values from these enthalpies, the standard molar enthalpies of formation in the gas were obtained. From the standard molar enthalpies of formation of the gaseous chelates the homolytic 191.9 ± 3.6, 167.9 ± 3.1, 136.4 ± 2.5, 174.3 ± 3.0 and 189.1 ± 3.9 kJ mol^{-1}, and heterolytic 938.1 ± 3.6, 961.9 ± 3.1, 993.5 ± 2.7, 1003.0 ± 3.0 and 1047.3 ± 3.9 kJ mol^{-1}, mean indium–sulphur bond-dissociation enthalpies were calculated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Indium; Dialkyldithiocarbamate; Enthalpy; Calorimetry; Bond-dissociation

1. Introduction

The aim of the present report is to investigate the synthesis of indium(III) dialkyldithiocarbamates, from acidic solutions of In(III), with the dialkylammonium salt of the ligand. These experiments succeeded in high yield one-step-one-pot synthesis of these complexes.

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 the 1960's [1] and the first review including thermal data and solution thermochemistry of metal dithiocarbamate complexes and related compounds was published in 1981 [2,3] followed by another recent review in 1992 [4].

This publication focuses on the thermochemical data for chelates of dialkyldithiocarbamate of In(III). These results are used to investigate the effect of the

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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 vacuum or in a dry-box in an atmosphere of dried nitrogen for air-sensitive compounds.

2.1. Chemical

The solvents used in all the preparations were distilled and stored over Linde 4A molecular sieves. Diethyl, di-*n*-propyl, di-*iso*-propyl, di-*n*-butyl, di-*iso*-butylamine (Merck) and carbondisulfide (Merck) were purified and distilled. Indium metal (Aldrich) was used as supplied, dried acetone was chosen as the calorimetric solvent due to its ability to dissolve the chlorides, ligand and chelates.

2.2. Preparations

The salts ammonium chloride, R_2NH_2Cl, and dialkylammonium dialkyldithiocarbamate, $R_2NH_2S_2CNR_2$, were synthesized with $R = C_2H_5$, n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9. Their analysis and melting points were in complete agreement with their formulation and reported melting points [5–8].

Reaction of acidic solution of In(III) with dialkylammonium dialkyldithiocarbamate to produce $In(S_2CNR_2)_3$, ($R = C_2H_5$, n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9) metallic indium (0.50 g, 4.35 mmol) was dissolved in 2.0 cm^3 HCl (12.0 mol dm^{-3}). The solution was diluted to 10.0 cm^3 and the pH was adjusted to 3–4 with aqueous sodium hydroxide. To this solution was added $R_2NH_2R_2NCS_2$ (13.05 mmol) prepared from 26.1 mmol of R_2NH with excess of CS_2 (8.0 cm^3, 132.4 mmol) in 8.0 cm^3 of acetone. Immediately, after addition, a white precipitate was formed. Volatiles were removed under vacuum until the volume reach half of the initial volume. The white solid was filtered and recrystallized from chloroform/ethanol to produce $In(S_2CNR_2)_3$ as colourless crystals. Yields based on the initial amount of indium gave 74.9% (C_2H_5), 73.2% (n-C_3H_7), 70.9% (i-C_3H_7), 78.6% (n-C_4H_9) and 73.9% (i-C_4H_9).

2.3. Physical measurements

Indium in all compounds was determined by back titration of EDTA with thorium nitrate [9]. Microanalysis (C, H, N) were carried out with a Perkin-Elmer elemental analyser. Infrared spectra were recorded as KBr pellets on a BOMEM, model MB-102 spectrophotometer. ^1H and ^{13}C NMR data were obtained in a Varian Gemini, 300 MHz, spectrometer. The melting temperatures for all compounds were determined by means of a MICROQUíMICA, model MQAPE-301 apparatus. Thermogravimetric curves were obtained using a SHIMADZU model TGA-50 thermobalance, at a heating rate of 10°C min^{-1} in a dynamic atmosphere of dry nitrogen flux of 0.83 ml s^{-1} and the temperature range of 445–695 K and mass spectra of the ligand and chelates on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV, at 523 K for analysis of the residues of thermal decomposition a X-ray SIEMENS model D-5000 difractor was used.

2.4. Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 isoperibolic precision calorimeter system as previously described [10]. 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 [5,11].

3. Results and discussion

The preparation of dialkyldithiocarbamates of In(III) complexes of general formula $In(S_2CNR_2)_3$,

Table 1
Elemental analysis data, percentage values are indicated in parenthesis and melting point

Chelates	In (%)	C (%)	H (%)	N (%)	Melting point (°C)
$In(S_2CNEt_2)_3$	20.6(20.6)	32.24(32.12)	4.57(4.41)	7.48(7.51)	249
$In(S_2CNPr^n_2)_3$	17.5(17.9)	38.12(39.10)	6.23(6.50)	6.39(6.53)	198
$In(S_2CNPr^i_2)_3$	17.4(17.9)	39.46(39.14)	6.53(6.53)	6.59(5.95)	288
$In(S_2CNBu^n_2)_3$	16.0(15.8)	44.81(44.58)	7.14(7.49)	5.77(5.77)	170
$In(S_2CNBu^i_2)_3$	16.0(15.8)	44.66(44.59)	7.16(7.49)	5.75(5.77)	171

($R = C_2H_5$, n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9), from the reaction of acid solutions of salts with metallic indium, certainly provides an alternative and convenient route to obtain this class of chelates, as it is listed in Table 1. The products are obtained in a one-step-one-pot high yield synthesis. The method is obviously simpler than that normally used, which is generally based on the reaction of indium trichloride with dialkyldithiocarbamate salts [12].

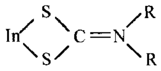
Elemental analysis data for $In(S_2CNR_2)_3$ compounds are listed in Table 1 and the results conformed to the proposed molecular formula. The melting points are listed in the Table 1. The most prominent feature in the IR spectra of these compounds is related to the ν(C–N) at the dialkyldithiocarbamato ligand. The observed frequencies are: 1499 $In(S_2CNEt_2)_3$, 1492 for $In(S_2CNPr^n_2)_3$, 1460 for $In(S_2CNPr^i_2)_3$, 1494 for $In(S_2CNBu^n_2)_3$ and 1484 cm^{-1} for $In(S_2CNBu^i_2)_3$. The normal range of absorption of a C–N single bound stretching lies near 1250 cm^{-1}. However, these bands were assigned [13,14] previously at 1480–1550 cm^{-1} region for a great number of dithiocarbamate complexes as a vibration of a polar C=N stretching mode.

The three bidentate dialkyldithiocarbamate ligands impose an hexacoordinated arrangement around the indium atom. The structures of tris(diethyldithiocarbamate) of indium $In[S_2CN(C_2H_5)_2]_3$, [13] and related piperidine analogue, have been determined [15] and easily corroborate with this proposition. Thus, in both cases it was found that the InS_6 kernel is a highly distorted octahedral with symmetry near D_3. It seems reasonable to expect that similar structures can be found for the dialkyldithiocarbamate of indium(III) compounds synthesized.

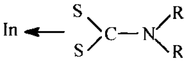
A final interesting feature related to the decrease of C=N stretching frequencies with the increase in size of the R groups. On the other hand, similar trend was also observed [14] for a series of $Cu(S_2CNR_2)_2$ complexes.

The NMR (^1H and ^{13}C) data for the $In(S_2CNR_2)_3$ compounds are displayed in Table 2. The spectra confirm the proposed ligands in five of the $In(S_2CNR_2)_3$ ($R = C_2H_5$, n-C_3H_7, n-C_4H_9, i-C_4H_9), by presenting normal splitting pattern for the corresponding R group. However, a very unusual NMR spectra was observed for the *iso*-propyl derivative ($R = i$-C_3H_7). The ^1H NMR exhibits three very broad signals: a set of two singlets centered at ca. 5.10 and 4.00 ppm integrating 1H that can reasonably be attributed to methyne proton; the third centered at ca. 1.5 ppm integrating 6H which is attributed to the methyl protons of the *iso*-propyl ligand. In this connection, ^{13}C spectrum also showed two broad signals centered at 50.6 and 60.4 ppm attributed to the methyne carbon atom and a sharp signal at 19.8 ppm for the methyl carbon of the isopropyl ligand.

These values suggest that the broadening of the signals is due to unresolved coupling with the nitrogen ($I = 1$) of the di-*iso*-propyldithiocarbamate ligand. The existence of two signals for the methyne protons and carbon seems to suggest two different co-ordination modes of the ligand in solution; as known for dialkyldithiocarbamates [16] that can bond to the central metal atom in a conventional bidentate configuration,



involving two σ bonding orbitals of the metal or as a three center bonded ligand,



in which is involved a single metallic σ orbital.

Table 2
^{1}H and ^{13}C NMR spectra (ppm) for the chelates

Chelates	^{1}H[a]	^{13}C[b]	Assignment
$In(S_2CNEt_2)_3$	3.76(q, 2H)	50.6	$N–CH_2–CH_3$
	1.26(t, 3H)	12.1	$N–CH_2–CH_3$
		[c]	CS_2
$In(S_2CNPr^n_2)_3$	3.62(t, 2H)	58.0	$N–CH_2–CH_2–CH_3$
	1.75(Sext, 2H)	20.2	$N–CH_2–CH_2–CH_3$
	0.85(t, 3H)	11.2	$N–CH_2–CH_2–CH_3$
		202.2	CS_2
$In(S_2CNPr^i_2)_3$	5.15–5.00(br) 1H; 4.05–3.90(br) 1H	50.6(br); 60.4(br)	$–CH(CH_3)_2$
	1.8–1.1(br) 6H	19.8	$–CH(CH_3)_2$
		200.9	CS_2
$In(S_2CNBu^n_2)_3$	3.66(t[d], 2H)	56.2	$N–CH_2–CH_2–CH_2CH_3$
	1.70(Quint, 2H)	28.8	$N–CH_2–CH_2–CH_2CH_3$
	1.30(q, 2H)	20.1	$N–CH_2–CH_2–CH_2–CH_3$
	0.90(t, 3H)	13.6	$N–CH_2–CH_2–CH_2–CH_3$
		201.8	CS_2
$In(S_2CNBu^i_2)_3$	3.57(d, 2H)	63.8	$N–CH_2–CH(CH_3)_2$
	2.36(m, 1H)	27.0	$N–CH_2–CH(CH_3)_2$
	0.89(d, 6H)	20.3	$N–CH_2–CH(CH_3)_2$
		203.8	CS_2

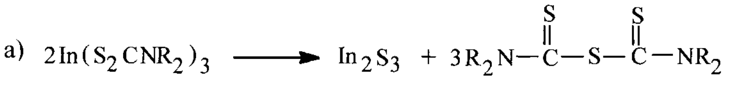
[a] In $CDCl_3$ solutions.
[b] In ppm from TMS.
[c] Not detected.
[d] Distorted triplet.

Table 3 gives TG/DTG data for $In(S_2CNR_2)_3$ compounds. One-step weight loss curves were obtained in every case. The nature of the final residue obtained upon heating, suggest two different pathways of decomposition, depending on the R group on the dithiocarbamate ligand. When $R = i\text{-}C_3H_7$ and $n\text{-}C_4H_9$, the decomposition occurs leading to In_2S_3 residue, agreement with results of X-ray. If $R = C_2H_5$, $n\text{-}C_3H_7$, and $i\text{-}C_4H_9$, the X-ray has confirmed the presence of an In as a main phase of the final residue, although there is no perfect agreement between the experimental and calculated values on the amount of the final residue for the *n*-propyl and *iso*-butyl derivatives, due the presence of small amounts of oxides, probably formed with oxygen present in the nitrogen.

The removed volatile compounds upon heating were not characterized, nevertheless, for the observed final residues the following equations for the thermal decomposition can be proposed:

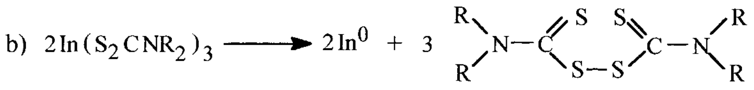
Table 3
TG/DTG data, indicating the percentage of weight loss, found and (calculated), the proposed residue, TG temperature range and DTG temperature peak

Chelates	Weight loss (%)	Proposed residue	Found (calculated) (%)	Temperature range (°C)	DTG temperature peak (°C)
$In(S_2CNEt_2)_3$	80.85	In^0	19.15(20.60)	265–378	352
$In(S_2CNPr^n_2)_3$	79.34	In^0	18.66(17.90)	239–385	350
$In(S_2CNPr^i_2)_3$	74.36	In_2S_3	25.64(25.35)	280–346	316
$In(S_2CNBu^n_2)_3$	78.99	In_2S_3	21.01(22.42)	265–391	360
$In(S_2CNBu^i_2)_3$	88.69	In^0	14.31(15.80)	264–393	372



$$\text{a)}\ 2In(S_2CNR_2)_3 \longrightarrow In_2S_3 + 3R_2N{-}\overset{\overset{S}{\|}}{C}{-}S{-}\overset{\overset{S}{\|}}{C}{-}NR_2$$

(R = i-C_3H_7 and n-C_4H_9).



(R = -C_2H_5, n-C_3H_7 and i-C_4H_9).

It is worth mentioning that reaction (b) indicates the decomposition of tris(diethyldithiocarbamate) of indium to metal and the corresponding dialkylthiuram disulfide.

The mass spectra of the complexes revealed the presence of the parent ions, except for the $In(S_2CNPr^{i}_{2})_3$, with the following order of stability: $In(S_2CNPr^{n}_{2})_3 > In(S_2CNBu^{i}_{2})_3 > In(S_2CNBu^{n}_{2})_3 > In(S_2CNEt_2)_3$.

The standard molar enthalpy of reaction, $\Delta_r H^0_m$, was obtained at $T = 298.15$ K, from the reaction-solution enthalpies, $\Delta_i H^0_m$, of each reagent and product dissolved sequentially in acetone (Table 4), where a strict control of stoichiometry was mentioned, for the following general reaction [5–8]:

$$InCl_3(cr) + 3NH_2R_2S_2CNR_2(cr) \rightarrow In(S_2CNR_2)_3(cr) + 3NH_2R_2Cl(cr);\quad \Delta_r H^0_m. \tag{1}$$

The standard molar enthalpy for each reaction was calculated from these tabulated values by applying a convenient thermochemical cycle, individual enthalpy values are listed in Table 5.

The standard molar enthalpies of formation of the crystalline chelates shown in Table 5, were determined from $\Delta_r H^0_m$ and the respective standard molar enthalpies of formation of the indium chloride [17], ligands [18] and ammonium chlorides [19], by using expression (2), with the auxiliary data listed in Table 6.

Table 4
Standard molar enthalpies (kJ mol^{-1}) of solution-reaction, at 298.15 K

Reactant	Solvent	Solution	Number of experiments	$\Delta_i H^0_m$
$3Et_2NH_2S_2CNEt_2$(cr)	Acetone	A_1	6	48.98 ± 0.72
$InCl_3$(cr)	A_1	A_2	6	−211.06 ± 1.77
$In(S_2CNEt_2)_3$(cr)	Acetone	A_3	6	36.16 ± 0.50
$3Et_2NH_2Cl$(cr)	A_3	A_4	6	33.10 ± 0.86
$3Pr^{n}_{2}NH_2S_2CNPr^{n}_{2}$(cr)	Acetone	B_1	6	54.41 ± 0.16
$InCl_3$(cr)	B_1	B_2	6	−226.48 ± 1.99
$In(S_2CNPr^{n}_{2})_3$(cr)	Acetone	B_3	6	35.59 ± 2.03
$3Pr^{n}_{2}NH_2Cl$(cr)	B_3	B_4	5	40.35 ± 1.47
$3Pr^{i}_{2}NH_2S_2CNPr^{i}_{2}$(cr)	Acetone	C_1	6	51.17 ± 0.54
$InCl_3$(cr)	C_1	C_2	6	−208.42 ± 2.19
$In(S_2CNPr^{i}_{2})_3$(cr)	Acetone	C_3	5	13.20 ± 0.51
$3Pr^{i}_{2}NH_2Cl$(cr)	C_3	C_4	6	21.48 ± 0.86
$3Bu^{n}_{2}NH_2S_2CNBu^{n}_{2}$(cr)	Acetone	D_1	6	68.12 ± 0.38
$InCl_3$(cr)	D_1	D_2	5	−248.75 ± 2.11
$In(S_2CNBu^{n}_{2})_3$(cr)	Acetone	D_3	6	37.50 ± 1.51
$3Bu^{n}_{2}NH_2Cl$(cr)	D_3	D_4	6	24.90 ± 0.41
$3Bu^{i}_{2}NH_2S_2CNBu^{i}_{2}$(cr)	Acetone	E_1	5	56.92 ± 0.12
$InCl_3$(cr)	E_1	E_2	5	−216.91 ± 2.19
$In(S_2CNBu^{i}_{2})_3$(cr)	Acetone	E_3	6	42.87 ± 0.80
$3Bu^{i}_{2}NH_2Cl$(cr)	E_3	E_4	5	50.74 ± 0.64

Table 5
Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ mol^{-1} K^{-1}) and temperatures (K) for the chelates

Parameters	$In(S_2CNEt_2)_3$	$In(S_2CNPr^n_2)_3$	$In(S_2CNPr^i_2)_3$	$In(S_2CNBu^n_2)_3$	$In(S_2CNBu^i_2)_3$
$-\Delta_r H^0_m$	231.34 ± 2.15	248.01 ± 3.20	191.93 ± 2.47	243.03 ± 2.65	253.60 ± 2.42
$-\Delta_f H^0_m(cr)$	436.9 ± 8.4	676.3 ± 6.6	725.6 ± 5.6	806.8 ± 6.4	799.0 ± 5.9
$-\Delta^l_{cr} H^0_m$	30.92 ± 0.82	37.74 ± 2.14	30.64 ± 1.89	40.93 ± 2.02	28.87 ± 1.16
$-\Delta^g_l H^0_m$	140.25 ± 2.21	200.97 ± 1.89	123.65 ± 2.34	201.7 ± 2.81	137.33 ± 1.99
T_{fus}	522.7 ± 1.1	471.5 ± 1.9	561.4 ± 2.5	443.6 ± 2.2	444.1 ± 3.0
T_{vap}	611.1 ± 2.1	589.4 ± 2.7	740.8 ± 3.4	607.2 ± 3.1	594.3 ± 2.4
$C_{p,m}(cr)$	0.938 ± 0.051	1.107 ± 0.033	1.862 ± 0.051	1.367 ± 0.039	1.505 ± 0.063
$C_{p,m}(l)$	0.866 ± 0.073	1.980 ± 0.112	0.680 ± 0.085	1.947 ± 0.097	1.206 ± 0.198
$C_{p,m}(g)$	0.9 ± 0.1	1.0 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	1.3 ± 0.1
$\Delta^g_{cr} H^0_m$	176.7 ± 3.3	372.8 ± 3.4	279.5 ± 3.5	358.2 ± 3.2	182.0 ± 3.3
$-\Delta_f H^0_m(g)$	260.2 ± 9.0	303.5 ± 7.4	446.1 ± 6.6	448.6 ± 7.1	617.0 ± 6.8
$-\Delta_{ho} H^0_m$	1151.2 ± 21.6	1002.2 ± 18.5	818.7 ± 15.9	1045.6 ± 18.1	1135.0 ± 23.9
$-\Delta_{he} H^0_m$	5628.7 ± 21.6	5771.3 ± 18.4	5961.0 ± 18.1	6018.1 ± 18.1	6289.9 ± 29.9
$\langle D \rangle$(In–S)	191.9 ± 3.6	167.0 ± 3.1	136.4 ± 2.5	174.3 ± 3.0	189.1 ± 3.9
$\langle D' \rangle$(In–S)	938.1 ± 3.6	961.9 ± 3.1	993.5 ± 2.7	1003.0 ± 3.0	1048.3 ± 3.9

$$\begin{aligned}\Delta_f H^0_m[In(S_2CNR_2)_3](cr) &= \Delta_r H^0_m - 3\Delta_f H^0_m(NH_2R_2Cl)(cr) \\ &\quad + \Delta_f H^0_m(InCl_3)(cr) \\ &\quad + 3\Delta_f H^0_m(NH_2R_2S_2CNR_2)(cr). \qquad (2)\end{aligned}$$

Table 6
Auxiliary data (kJ mol^{-1})

Species	$\Delta_f H^0_m$	Reference
$InCl_3(cr)$	−537.2 ± 3.1	[17]
$Et_2NH_2S_2CNEt_2(cr)$	−249.2 ± 2.2	[18]
$Et_2NH_2Cl(cr)$	−359.73 ± 1.22	[19]
$Pr^n_2NH_2S_2CNPr^n_2(cr)$	−353.20 ± 1.30	[18]
$Pr^n_2NH_2Cl(cr)$	−389.50 ± 1.00	[8]
$Pr^i_2NH_2S_2CNPr^i_2(cr)$	−349.6 ± 1.3	[18]
$Pr^i_2NH_2Cl(cr)$	−350.77 ± 0.15	[8]
$Bu^n_2NH_2S_2CNBu^n_2(cr)$	−461.3 ± 1.6	[18]
$Bu^n_2NH_2Cl(cr)$	−452.44 ± 0.39	[8]
$Bu^i_2NH_2S_2CNBu^i_2(cr)$	−463.8 ± 1.4	[18]
$Bu^i_2NH_2Cl(cr)$	−461.07 ± 0.50	[8]
In(g)	243.3 ± 2.6	[17]
$In^{3+}(g)$	5322.0 ± 1.7	[17]
$Et_2NCS^{\cdot}_2(g)$	215.9 ± 6.5	[10]
$Et_2NCS^-_2(g)$	15.5 ± 6.5	[10]
$Pr^n_2NCS^{\cdot}_2(g)$	151.8 ± 5.6	[6]
$Pr^n_2NCS^-_2(g)$	48.6 ± 5.6	[6]
$Pr^i_2NCS^{\cdot}_2(g)$	43.1 ± 4.9[a]	
$Pr^i_2NCS^-_2(g)$	64.3 ± 4.9[a]	
$Bu^n_2NCS^{\cdot}_2(g)$	117.9 ± 5.5	[11]
$Bu^n_2NCS^-_2(g)$	82.5 ± 5.5	[11]
$Bu^i_2NCS^{\cdot}_2(g)$	87.5 ± 7.6	[5]
$Bu^i_2NCS^-_2(g)$	112.9 ± 7.6	[5]

[a] Obtained in this work.

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 standard molar enthalpies of vaporization were determined through estimative methods [5–8,20]. The standard molar enthalpies of fusion and heat capacities for the solid and liquid phases of the complexes were determined by mean DSC technique. However, for the gas phase these quantities were estimated [5–8,21]. A complete series of these values obtained are listed in Table 5, together with the standard molar enthalpies of sublimation. These values were calculated by applying all these auxiliary data in Eq. (3) and consequently the standard molar enthalpies of formation in the gas phase, listed in Table 5, were calculated.

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

The auxiliary data listed in Table 6 enables the calculation of the mean enthalpy of indium–sulphur bond [5–8,11] for homolytic, $\langle D \rangle(In-S) = \Delta_{ho} H^0_m/6$ and for heterolytic, $\langle D' \rangle(In-S) = \Delta_{he} H^0_m/6$, values which are listed in Table 5.

The results presented in Table 5 show that $\langle D \rangle$(In–S) and $\langle D' \rangle$(In–S) values follow a sequence not much expected. This behavior 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 metal, which can be reflected on the homolytic and heterolytic bond enthalpy parameters, than with that of the ligand chain bonded to the co-ordination sites. Similar conclusion was observed before with dialkyldithiocarbamate chelates of zinc-group elements [6,7,10].

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 [11]. In that kind of correlation it was observed a decrease in these thermochemical data with the increase of the atomic number of these elements.

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