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N,N'-Dialkyldithiocarbamate chelates of indium(III): alternative synthetic routes and thermodynamics characterization

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Abstract

Alternative synthetic routes to prepare N,N'-dialkyldithiocarbamate complexes of indium(III), $In(S_2CNR_2)_3$ ($R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9) from the metallic element and from indium monohalides, InX(X = Cl, Br and I) were established. The proposed mechanism of reaction involving InX considering a ligand redistribution reaction of $XIn(S_2C–NR_2)_2$ initially produced, which could be derived from the insertion of InX into sulfur–sulfur bond of the tetralkylthiuram disulfide. The thermal decomposition of the $In(S_2CNR_2)_3$ ($R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9) compounds was investigated by the thermogravimetric technique, where two pathways were detected, depending on the dialkyldithiocarbamato ligand. The first step leads to indium metal, or alternatively In_2S_3, as the final residue for $R = C_2H_5$, n-C_3H_7, i-C_4H_9 and for $R = CH_3$, i-C_3H_7, n-C_4H_9, respectively. The corresponding standard molar enthalpies of sublimation of all compounds were determined by means of differential scanning calorimetry and methods of estimation.

Keywords: Synthesis; Thermodynamic characterization; Indium; Dialkyldithiocarbamate

1. Introduction

Synthetic routes to obtain complexes from oxidation of the metallic element, in the presence of the ligand dispersed in a given medium, are always of great interest from the chemistry point of view, because this method frequently results in the one-step-one-pot procedure for preparation of the desired substance.

The first white complex isolated in 1942 was indium(III) diethyldithiocarbamate, which was prepared by reacting the weakly acid solution of indium salt with sodium diethyldithiocarbamate [1]. Since then, a set of derivative compounds were synthesized and the great majority of reports [2,3] deal with a number of publications, leading to such kind of complexes obtained by adding the corresponding dialkyldithiocarbamate salts to a solution of indium(III) chloride, which is a highly toxic, corrosive and hygroscopic substance.

The aim of the present report is to investigate the synthesis of indium(III) dialkyldithiocarbamates from acidic solutions of indium(III), which complexes are easily synthesized by dissolving the metallic element in hydrogen chloride. These experiments succeeded in providing high yield one-step-one-pot synthesis of these substances.

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In the course of this investigation, a new course of synthesis was applied, where the compound indium(III) dimethyldithiocarbamate can also be isolated by oxidation of indium in the presence of tetramethylthiuram disulfide, when both reagents are refluxed in xylene. Identically, indium(III) dialkyldithiocarbamates (alkyl = methyl or ethyl) were prepared by the oxidation of indium(I) bromide by refluxing in xylene with the corresponding tetraalkylthiuram disulfide. The proposed mechanism of this kind of reaction is supposed to be a ligand redistribution reaction.

Further, a new method that is related to the oxidation of a sacrificial indium anode in an electrochemical cell, containing the corresponding tetraalkyl thiuram disulfide, can also lead to reasonable yields of $In(S_2CNR_2)_3$ ($R = CH_3$, C_2H_5) complexes.

2. Experimental

2.1. Chemical

Indium metal (Aldrich) was used as supplied. Acetonitrile was refluxed over CaH_2 and distilled before use. Xylene was dried over sodium and distilled from the blue ketyl form. Indium monohalides were prepared by heating the corresponding trihalide and indium metal in a sealed tube [4] at 450°C.

2.2. Preparations

Typical procedures for all preparations are described below:

(a) Reaction of acidic solution of In(III) with dialkylammonium dialkyldithiocarbamate to produce $In(S_2CNR_2)_3$ ($R = CH_3$, C_2H_5, n-C_3H_7, 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 $(R_2NH_2)^+(R_2NCS_2)^-$ (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 vacuo until the volume reaches half of the initial volume. The white solid was filtered and recrystallized in chloroform/ethanol to produce $In(S_2C\text{–}NR_2)_3$ in the form of colorless crystals. Yields based on the initial amount of indium gave for $R = CH_3$, the value 78.6%; $R = C_2H_5$, 74.9%; $R = n$-C_3H_7, 73%, $R = i$-C_4H_9, 73.9%.

(b) Reaction of indium metal with $(CH_3)_2NC(S)S\text{–}S(S)CN(CH_3)_2$ to prepare $In[S_2CN(CH_3)_2]_3$. Metallic indium (0.20 g, 1.74 mmol) and $(CH_3)_2NC(S)S\text{–}S(S)CN(CH_3)_2$ (0.62 g, 2.59 mmol) were refluxed in 30.0 cm^3 of xylene for 24 h. The solid (0.40 g) formed was filtered while the solution was hot, recrystallized in chloroform/ethanol mixture to yield 0.32 g (0.67 mmol) of $In[S_2CN(CH_3)_2]_3$. The xylene solution was cooled to room temperature; at this stage, crystals of $In[S_2CN(CH_3)_2]_3$ start to precipitate from the solution; the vessel was kept at −18°C for two days and the crystals filtered off to yield additional 0.21 g (0.44 mmol) of the same product. Total yield 0.53 g (1.12 mmol, 64.4%).

(c) Electrochemical preparation of $In(S_2C\text{–}NR_2)_3$ ($R = CH_3$, C_2H_5). The method of preparation of these compounds was essentially the same as that used in our previous publications [6,7]. The solution phase (ca. 5 mmol) of the corresponding tetraalkylthiuram disulfide was dissolved in 50.0 cm^3 of acetonitrile containing 50.0 mg of tetraethylammonium perchlorate as the supporting electrolyte, then poured into a 100.0-cm^3 round-bottomed flask with a Schlenk arm. A rod of indium metal was suspended through a rubber septum to form the anode of the cell, and consequently, a platinum wire was the cathode. The electrolysis was conducted at a constant current of 30 mA (initial voltage ca. 12 V) for 173 and 114 min to give $(S_2CNMe_2)_2$ and $(S_2CNEt_2)_2$, respectively. At the end of this time, 385.5 mg (3.36 mmol) of indium had dissolved for the methyl compound and 241.8 mg (2.10 mmol) for the ethyl derivative. The products precipitated in the cell were collected, dried under vacuo and recrystallized in chloroform to yield 0.80 g (1.68 mmol, 50% based on the metal dissolved) of $In(S_2CNMe_2)_3$ and 0.75 g (1.34 mmol, 63.8%) of $In(S_2CNEt_2)_3$. The corresponding current efficiencies for the processes that lead to the methyl and ethyl derivatives were 1.04 and 0.99 mol F^{-1}.

(d) Reaction of InX (X = Cl, Br, I) with $(C_2H_5)_2NC(S)S\text{–}S(S)CN(C_2H_5)_2$. InX (5.0 mmol) and tetraethylthiuram disulfide (1.48 g, 5.0 mmol) were stirred in xylene (30.0 cm^3) for 30 h (X = Br, I) and 72 h (X = Cl). Slowly, the colored monohalides were consumed to yield a white solid. This solid was filtered and redissolved in 50.0 cm^3 of acetone : ethanol mixture, in a 1 : 1 proportion. This solution was kept standing and open to the air to allow evaporation of the solvent. The first crop of crystals that precipitated was shown to be $In[S_2CN(C_2H_5)_2]_3$ (X = Cl, 0.96 g, 1.71 mmol, 51.3%; X = Br, 0.93 g, 1.66 mmol, 49.8%; X = I, 1.01 g, 1.81 mmol, 54.3%). After crystal deposition, the solution again starts to separate more solid with increasing contents of halogen; these were removed by filtration until precipitation ceased. At this point, excess of pyridine (0.5 cm^3, 0.49 g, 6.18 mmol) is added to the final solution. This procedure leads to the precipitation of the pyridine adducts, such as, $InX_3(py)_n$ (X = Cl, $n = 3$; 0.11 g 0.24 mmoles, 14.5%; X = Br, $n = 3$; 0.32 g; 0.54 mmol, 32.5%; X = I; $n = 1.5$; 0.36 g; 0.59 mmol, 35.5%). Tris(di-isopropyldithiocarbamate) indium(III) and tris(di-*n*-butyldithiocarbamate)indium(III) used in the thermochemical studies were prepared from $InCl_3$ and the corresponding sodium dithiocarbamate.

2.3. Physical measurements

In all the compounds, indium was determined by back titration of EDTA with thorium nitrate [5]. Halide was analyzed by using Volhard's method, which is based on silver halide precipitation, and back titrated with potassium thiocyanate solution [5]. Microanalysis (C, H, N) was carried out with a Perkin–Elmer elemental analyzer. Infrared spectra were recorded as KBr pellets on a Bomem, model MB-102 spectrophotometer. ^1H and ^{13}C NMR data were obtained in Varian Gemini, 300 MHz, spectrometer. The melting temperatures for all compounds were determined by means of Microquímica, model MQAPF-301 apparatus. Residues of the thermal decomposition were analyzed using an X-ray Siemens model D-5000 diffractometer.

2.4. Thermochemical measurements

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 a 445–695 K range. The standard molar 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 10°C min^{-1}, purged with dry nitrogen flux of 0.83 mL s^{-1}.

3. Results and discussion

The preparation of the various dialkyldithiocarbamates of indium(III) of the general formula $In(S_2CNR_2)_3$, 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 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 dialkyldithiocarbamates salts [2,3]. Tris(dimethyldithiocarbamate) of indium(III) also can be prepared by heating indium metal and tetramethylthiuram disulfide, $Me_2NC(S)S–S(S)CNMe_2$, in xylene. The reaction of oxidation from the metallic element is very close to that employed [8] for the preparation of indium triiodide, InI_3, when indium and iodine are heated in the same solvent. Again, the reaction provides a useful route to yield the compound; particularly when one considers that the disulfide is a commercially available reagent. But,

Table 1
Elemental analysis data for $In(S_2CNR_2)_3$ compounds, for which percent values are indicated in parentheses

R	In	C	H	N
$In(S_2CNMe_2)_3$	25.2 (24.2)	22.87 (22.73)	3.23 (3.82)	8.75 (8.84)
$In(S_2CNEt_2)_3$	20.6 (20.6)	32.24 (32.1)	4.57 (%0.41)	7.48 (7.51)
$In(S_2CNPr_2{}^n)_3$	17.5 (179)	38.12 (39.1)	6.23 (6.50)	6.39 (6.53)
$In(S_2CNPr_2{}^i)_3$	17.4 (17.9)	39.46 (39.1)	6.53 (6.53)	6.59 (5.95)
$In(S_2CNB_2{}^n)_3$	16.0 (15.8)	44.81 (44.5)	7.14 (7.49)	5.77 (5.77)
$In(S_2CNBu_2{}^i)_3$	16.0 (15.8)	44.66 (44.5)	7.16 (7.49)	5.75 (5.77)

attempts to prepare the tris(diethyldithiocarmate) analog by the same method have failed.

A third method that provides a simple route to tris(dialkyldithiocarbamate) of indium(III) is an electrochemical synthesis. Again, the nature of the starting material, metallic indium, and the commercially available tetraalkylthiuram disulfides provides simplicity for this route. Preparation of tris(dimethyldithiocarbamate) of indium(III) with a 28% yield by the electrolysis of an acetone solution of $Me_2NC(S)S–S(S)CNMe_2$ followed by the oxidation of a sacrificial indium anode has been reported [9]. In the following, the same reaction in acetonitrile $In(S_2CNR_2)_3$ (R = methyl and ethyl) was used to prepare 50.0% and 63.4% yields, respectively.

The stoichiometry of the electrochemical reactions is indicated by the electrochemical efficiency, defined as moles of metal dissolved per Faraday of charge (E_F). The value of $E_F = 1.00 \pm 0.00\ \mathrm{mol\ F^{-1}}$ indicates the formation of the indium(I) species, $In(S_2CNR_2)$, as the primary product which is inserted into the sulfur–sulfur bond of the disulfide, $R_2NC(S)S–S(S)CNR_2$, present in the phase to produce the indium(III) species, $In(S_2CNR_2)_3$ as the final product. This description implies the following sequence of reactions:

$$\text{Cathode}:\ R_2NC(S)S–S(S)CNR_2 + 2e^- \rightarrow 2R_2NCS_2^-$$

$$\text{Anode}:\ 2R_2NCS_2^- + 2In \rightarrow In(S_2CNR_2) + 2e^-$$

$$\text{Phase}:\ In(S_2CNR_2) + R_2NC(S)S–S(S)CNR_2 \rightarrow In(S_2CNR_2)_3$$

This mechanistic description is supported in the published [10] electrochemical preparation of indium(III) thiolato complexes, $In(SR)_3$, from the reduction of the alkyldisulfide followed by the oxidation of a metallic indium anode, where a similar mechanism was proposed. The key step in this mechanism is the insertion of the indium(I) dialkyldithiocarbamate into the sulphur–sulphur bond of thiuram $R_2NC(S)S–S(S)CNR_2$; and again this is a known process of indium(I) species, such as indium monohalides, which are inserted [12] into sulfur–sulfur bonds of alkyl disulfides to produce the corresponding indium(III) derivatives, $XIn(SR)_2$.

$$InX + RS - SR \rightarrow XIn(SR)_2$$

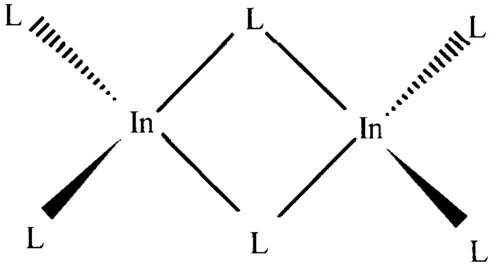
The reaction of InX with tetraethylthiuram disulfide, $Et_2NC(S)S–S(S)CNEt_2$, in xylene is followed by a slow consumption of the monohalide to yield a white precipitate. The process corresponds to an oxidative insertion of InX into the sulphur–sulphur bond of the thiuram as represented by:

$$InX + Et_2NC(S)S–S(S)CNEt_2 \rightarrow XIn(S_2CNEt_2)_2$$

However, the $XIn(S_2CNEt_2)_3$ compounds cannot be isolated. A tedious process of separation, involving recrystallization of the white solid initially formed in acetone/ethanol/pyridine mixture, produced tris-(diethyldithiocarmabate) of indium(III) and the corresponding pyridine adduct of InX_3. The nature of the products actually isolated implies the following ligand redistribution reaction:

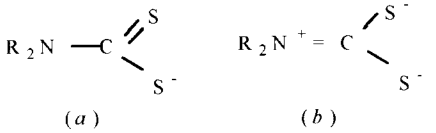
$$3XIn(S_2CNEt_2)_2 \rightarrow 2In(S_2CNEt_2)_3 + InX_3$$

Ligand redistribution reactions is a common feature in the chemistry of Group XIII compounds. The electron deficiency of InL_3 compounds causing strong intermolecular interactions, particularly when the ligand L has orbitals containing a lone pair of electrons. In many cases, dimeric structures appeared as indicated below:



This kind of structure has been proposed for InI_3 [12]. Mixed ligand systems, such as $L^1In(L^2)_2$, tend to redistribute among the corresponding $In(L^1)_3$ and $In(L^2)_3$ compounds through dimeric structures such as shown here. The preparation [11], confirmed by structure determination [13] of the pyridine adduct of $ClIn(O_2C–C_6H_5)_2$ is a very close example of such process.

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 most prominent feature in the IR spectra of these compounds is related to ν(C–N) at the dialkyldithiocarbamato ligand. The observed frequencies are: 1519 for $In(S_2CNMe_2)_3$, 1499 for $In(S_2CNEt_2)_3$. 1492 for $In(S_2CNPr_2{}^n)_3$, 1460 for $In(S_2CNPr_2{}^i)_3$, 1494 for $In(S_2CNBu_2{}^n)_3$ and 1484 cm^{-1} for $ln(S_2CNBu_2{}^i)_3$. The normal range of absorption of a C–N single-bond stretching lies near 1250 cm^{-1}. However, these bands were assigned [14,15] previously in the 1480–1550 cm^{-1} region as a vibration of a polar C=N stretching mode for a great number of dithiocarbamate complexes. The extension of the C–N stretching mode shifts to higher frequencies is associated to the contribution of the under resonance form (b) of the structure of the ligand when coordinated to the metal:

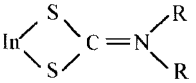


The C–N frequencies for $In(S_2CNR_2)_3$ compounds were all detected in the 1484–1519 cm^{-1} range. This fact implies that the dialkyldithiocarbamate ligand is present and is coordinated to the metal as a bidendate ligand, as proposed, in the form *b*. The three bidentate dialkyldithiocarbamate ligands impose a hexacoordinated arrangement around the indium atom. The structures of tris(diethyldithiocarbamate) of indium(III) [3] and the related pyperidine analog, $In[S_2CN(C_2H_5)_2]_3$, have been determined [16] and easily corroborate with this proposition. Thus, in both the 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 indium(III) dialkyldithiocarbamate compounds synthesized.

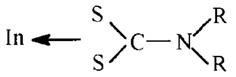
A final, interesting feature relates to the decrease of C=N stretching frequencies with the increase in size of the R groups. On the other hand, a similar trend was also observed [15] for a series of $Cu(S_2CNR_2)_2$ complexes.

The NMR (^1H and ^{13}C) data for the $In(Sr_2CNR_2)_3$ compounds are displayed at Table 2. The spectra confirm the proposed ligands in five of the $In(S_2CNR_2)_3$ (R = $-CH_3$, $-C_2H_5$, *n*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9), by presenting normal splitting patterns for the corresponding R group. However, a very unusual NMR spectra for the isopropyl derivative (R = *i*-C_3H_7) was observed. The ^1H NMR exhibits three very broad signals: a set of two singlets centered at ca. 5.10 ppm 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 isopropyl ligand. In this connection, the ^{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-isopropyldithiocarbamate ligand. The existence of two signals for the methyne protons and carbon seems to suggest two different coordination 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-centered bonded ligand as follows: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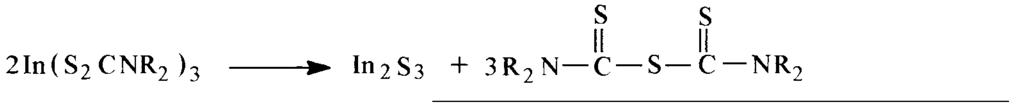
in which a single metallic σ-orbital is involved.

Table 3 gives TG/DTG data for $In(S_2CNR_2)_3$ compounds. One-step weight loss curve were obtained in every case. The nature of the final residue obtained upon heating, suggests two different pathways of decomposition, depending on the R group on the dithiocarbamate ligand. When R = $-CH_3$, *i*-C_3H_7 and *n*-C_4H_9, the decomposition leads to In_2S_3 residue, in agreement with the X-ray results. If R = $-C_2H_5$, *n*-C_3H_7, and *i*-C_4H_9, the X-ray confirmed the presence of In as a main phase of the final residue, although there was no perfect agreement between the experimental and calculated values on the amounts of the final residues for the *n*-propyl and *i*-butyl derivatives, due to 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:



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

Table 2
^1H and ^{13}C NMR spectra (ppm) for $In(S_2CNR_2)_3$ compounds

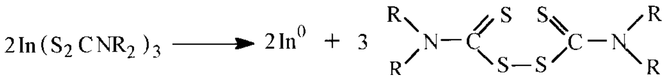
R	^1H [a]	^{13}C [b]	Assignment
$-CH_3$	3.40(s)	46.1	N-CH_3
		203.0	CS_2
$-CH_2CH_3$	3.76 (q,2H)	50.6	N-CH_2–CH_3
	1.26 (t,3H)	12.1	N-CH_2–CH_3
		— [c]	CS_2
$-CH_2CH_2CH_3$	3.62 (t,2H)	58.0	N-CH_2–CH_2–CH_3
	1.75 (sext, 2H)	20.2	N-CH_2–CH_2–CH_3
	0.85 (t,3H)	11.2	N-CH_2–CH_2–CH_3
		202.2	CS_2
$-CH(CH_3)_2$	5.15–5.00(br) 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
$-CH_2CH_2CH_2CH_3$	3.66(t[d],2H)	56.2	N-CH2—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_2CH_3
	0.90 (t,3H)	13.6	N-CH_2–CH_2–CH_2CH_3
		201.8	CS_2
$-CH_2CH(CH_3)_2$	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
TG/DTG data for $In(S_2CNR_2)_3$ compounds, indicating the percent weight loss, found and (calculated), the proposed residue, the temperature range (°C) and DTG peak temeprature (°C)

Complexe	Weight loss(%)	Proposed residue	Found (calculated)%	Temperature range/(°C)	DTG peak temperature/ (°C)
$In(S_2CNMe_2)_3$	65.74	In_2S_3	34.26 (34.32)	309–389	365
$In(S_2CNEt_2)_3$	80.85	In^0	19.15(20.60)	265–378	352
$In(S_2CNPr_2{}^n)_3$	79.34	In^0	20.66(17.90)	239–385	350
$In(S_2CNPr_2{}^i)_3$	74.36	In_2S_3	25.64 (25.35)	280–346	316
$In(S_2CNBu_2{}^n)_3$	78.99	In_2S_3	21.01 (22.42)	265–391	360
$In(S_2CNBu_2{}^i)_3$	88.69	In^0	11.31 (15.80)	264–393	372

where R = $-CH_3$, i-C_3H_7 and n-C_4H_9, and



[2]

where R = $-C_2H_5$, n-C_3H_7 and i-C_4H_9.

It is worth mentioning that equation [2] indicates the decomposition of tris(diethyldithiocarbamate) indium(III) to metal and the corresponding dialkylthiuram disulfide. This result seems to support the previous difficulty in preparing $In(S_2CNEt_2)_3$ by heating indium and diethylthiuram disulfide in xylene.

The standard molar enthalpies of sublimation, $\Delta_{cr}^{g}H_m^0$ listed in Table 4 were determined by means of differential scanning calorimetry (DSC) and estimative methods [17,18]. The DSC curves showed a sharp and a broad peak for all compounds. The first peak was identified as a fusion, occurring in the fusion temperatures, Table 4, from which the standard molar enthalpies of fusion were obtained, as shown the Table 4. The second peak, corresponding to vaporization, enables the determination of the vaporization temperatures and standard molar enthalpies of vaporization of the complexes, and are listed in Table 4. The heat capacities for the solid and liquid phases of the complexes, were determined by DSC, as shown Table 4. However, for the gas phase these quantities had to be estimated [17–19], because we were unsuccessful in subliming the compounds, Table 4. This methodology considers the substance as an ideal gas, it is valid for temperatures varying from 250 to 1500 K, which principles are based on the same spectroscopic and thermodynamic statistics data, by considering the modes of vibration of every chemical bond present in the molecule. The following equation is used to relate C_p^0 to the absolute temperature $C_p^o = a_i + b_{iT} + c_{iT}^2$, where a_i, b_i and c_i are constants determined from the generalized vibrational frequencies [20], according to the equations below for the following considered compounds:

$$C_{p,m}(g) = -0.027 + 1.326 \times 10^{-3}T - 0.658 \times 10^{-6}T^2\ (kJ\,mol^{-1}\,K^{-1})$$

for $In(S_2CNMe_2)_3$,

$$C_{p,m}(g) = -0.064 + 1.885 \times 10^{-3}T - 0.879 \times 10^{-6}T^2\ (kJ\,mol^{-1}\,K^{-1})$$

for $In(S_2CNEt_2)_3$,

$$C_{p,m}(g) = -0.102 + 2.448 \times 10^{-3}T - 1.109 \times 10^{-6}T^2\ (kJ\,mol^{-1}\,K^{-1})$$

and for $In(S_2CNPr_2^n)_3$ and $In(S_2CNPr_2^i)_3$, and

$$C_{p,m}(g) = -0.141 + 3.004 \times 10^{-3}T - 1.332 \times 10^{-6}T^2\ (kJ\,mol^{-1}\,K^{-1})$$

for $In(S_2CNBu_2^n)_3$ and $In(S_2CNBu_2^i)_3$.

Table 4
Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ mol^{-1} K^{-1}) and temperatures for $In(S_2CNR_2)_3$ compounds

Parameter	InL_1 [a]	InL_2 [b]	InL_3 [c]	InL_4 [d]	InL_5 [e]	InL_6 [f]
$\Delta_{cr}{}^{l}H_m^0$	166.71 ± 1.01	30.92 ± 0.82	37.74 ± 2.14	301.64 ± 1.89	40.93 ± 2.02	28.87 ± 1.16
$\Delta_l^g H_m^0$	169.17 ± 1.17	140.25 ± 2.21	200.97 ± 1.89	283.65 ± 2.34	201.7 ± 2.81	137.33 ± 1.99
T_{fus}	621.4 ± 2.1 [a]	522.7 ± 1.1	471.5 ± 1.9	561.4 ± 2.5	443.6 ± 2.2	444.1 ± 3.0
T_{vap}	776.1 ± 2.9	611.1 ± 2.1	589.4 ± 2.7	740.8 ± 3.4	607.2 ± 3.1	594.3 ± 2.4
$C_{p,m(cr)}$	0.625 ± 0.046	0.773 ± 0.051	1.107 ± 0.033	1.862 ± 0.051	1.367 ± 0.039	0.795 ± 0.063
$C_{p,m(l)}$	0.482 ± 0.081	0.866 ± 0.073	1.980 ± 0.112	0.680 ± 0.085	1.947 ± 0.097	1.077 ± 0.198
$C_{p,m(g)}$	0.6 ± 0.1	0.8 ± 0.1	1.0 ± 0.1	1.3 ± 0.1	1.3 ± 0.1	1.280 ± 0.95
$\Delta_{cr}^{g}H_m$	310.8 ± 3.6	176.6 ± 3.3	371.6 ± 3.4	128.1 ± 3.5	364.9 ± 3.2	75.63 ± 3.3

[a] CH_3.
[b] C_2H_5.
[c] n-C_3H_7.
[d] i-C_3H_7.
[e] n-C_4H_9.
[f] i-C_4H_9.

All these quantities are listed in Table 4, and the application of all these auxiliary quantities to the expression below resulted in the standard enthalpies of sublimation [18,19] of these chelates, Table 4:

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{0} = \int_{298\,\mathrm{K}}^{T_{\mathrm{fus}}} C_{\mathrm{p}}(s)\mathrm{d}T + \Delta_{\mathrm{cr}}^{l}H_{\mathrm{m}}^{0} + \int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} C_{\mathrm{p}}(l)\mathrm{d}T + \Delta_{l}^{\mathrm{g}}H_{\mathrm{m}}^{0} + \int_{T_{\mathrm{vap}}}^{T_{298\,\mathrm{K}}} C_{\mathrm{p}}(g)\mathrm{d}T$$

The main purpose of this thermochemical study is the determination of the properties of these chelates in the gaseous phase, whence it is possible to obtain the metal–sulphur bond enthalpy. Due to the inherent difficulty in subliming these complexes an application of the DSC technique was necessary for these determinations [18,19].

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