

# Gallium and indium dithiocarboxylates: Synthesis, spectroscopic characterization and structure of $[\text{MeGa}(\text{S}_2\text{Ctol})_2]$

Shamik Ghoshal<sup>a</sup>, Vimal K. Jain<sup>a,\*</sup>, Dimple P. Dutta<sup>a</sup>,  
Prasad P. Phadnis<sup>b</sup>, Munirathinam Nethaji<sup>b</sup>

<sup>a</sup> Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

<sup>b</sup> Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 5 September 2006; received in revised form 14 September 2006; accepted 14 September 2006

Available online 19 September 2006

## Abstract

Several gallium and indium dithiocarboxylate complexes of the type  $[\text{Me}_n\text{M}(\text{S}_2\text{CR})_{3-n}]$  ( $M = \text{Ga}, \text{In}; n = 0, 1, 2; R = \text{phenyl (Ph), } p\text{-tolyl (tol), mesityl (Mes)}$ ) have been synthesized. These complexes were characterized by elemental analysis, IR, UV–vis and NMR ( $^1\text{H}, ^{13}\text{C}\{^1\text{H}\}$ ) spectroscopy. Structure of  $[\text{MeGa}(\text{S}_2\text{Ctol})_2]$  was established by X-ray crystallography. The gallium atom adopts a distorted five coordinate geometry which is intermediate between trigonal bipyramidal and square pyramidal configurations. The complex  $[\text{Me}_2\text{InS}_2\text{Ctol}]$  underwent a two-step thermal decomposition leading to the formation of tetragonal  $\beta\text{-In}_2\text{S}_3$ .  
© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Gallium; Indium; Dithiocarboxylates; NMR; X-ray;  $\text{In}_2\text{S}_3$

## 1. Introduction

Organometallic and classical complexes of group 13 elements, particularly Ga and In, with chalcogen ligands are of considerable recent interest due to their diverse structural features [1] and their relevance as molecular precursors for metal chalcogenides [2–5]. Thus a variety of gallium and indium complexes with thiolates [6], pyridine-2-thiolate [7], monothiocarboxylate [8], and dithiolates (xanthates [9–11], dithiocarbamates [12,13], diorganodithio-phosphinate/-phosphates [14–17]) have been synthesized and characterized. Organogallium and indium thiolates,  $[\text{R}_2\text{MSR}']_2$  and  $[\text{RM}(\text{SR}')_2]_2$ , are often isolated as dimers. The indium complexes have been employed as precursors for deposition of indium sulfide films, which in general contained a mixture of sulfides. The dithiolate complexes, in general, are monomeric. Both classical and organoindium xanthate and dithiocarbamate complexes have shown promising poten-

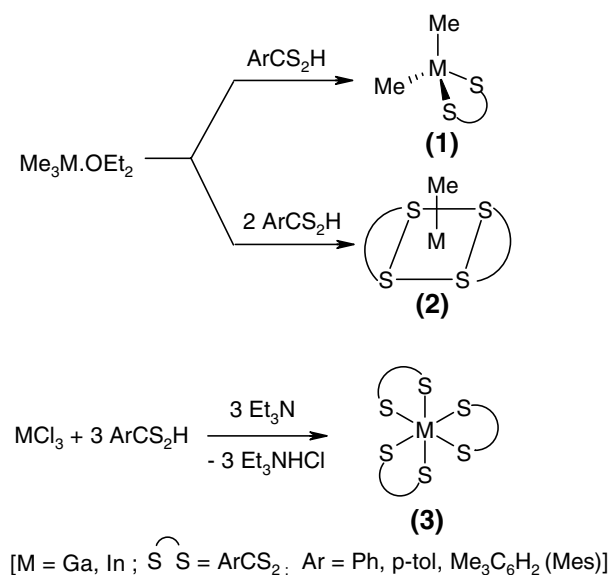
tial for the preparation of  $\beta\text{-In}_2\text{S}_3$  bulk, films and nanoparticles [4,10,11,13,17–19]. Structural aspects of tris chelates are now fairly well studied, whereas such investigations on organometallic dithiolates are limited to  $\text{Et}_2\text{In}(\text{S}_2\text{CNET}_2)$  [4]. The synthetic aspects of monoorganometal dithiolate are scanty [17,20].

The dithiocarboxylates are a versatile family of dithiolate ligands [21] and their gallium and indium complexes may have potential as molecular precursors for metal sulfides. In the light of the above and in pursuance of our work on gallium and indium dithiolate complexes we have synthesized dithiocarboxylates of gallium and indium and determined the structure of a monomethyl gallium dithiolate complex.

## 2. Results and discussion

Treatment of trimethyl gallium/indium etherate with dithiocarboxylic acids in 1:1 and 1:2 stoichiometry gave di- and mono-methyl metal complexes (Scheme 1). The reaction of  $\text{MCl}_3$  with the acids in 1:3 ratio in the presence

\* Corresponding author. Tel.: +91 22 2559 5095; fax: +91 22 2550 5151.  
E-mail address: [jainvk@barc.gov.in](mailto:jainvk@barc.gov.in) (V.K. Jain).



of triethylamine gave tris complexes. All these complexes are deep colored liquids/solids and are soluble in common organic solvents.

### 2.1. Spectroscopy

The electronic spectra of these complexes displayed two absorption bands in the region 304–462 nm attributable to  $\pi-\pi^*$  (shorter wavelength band) and  $n-\pi^*$  (longer wavelength absorption) of the thiocarbonyl group [22–26]. These absorptions appear at considerably shorter wavelengths (hypsochromic) than for the corresponding free acids, their dithioesters [23,24] (e.g.,  $\text{PhCS}_2\text{Ph}$ ,  $\lambda_{\text{max}}$  295, 527 nm) [24] and for triphenyl-germanium, -tin and -lead dithiobenzoates [25,26] (e.g.,  $\text{Ph}_3\text{GeS}_2\text{CPh}$ ,  $\lambda_{\text{max}}$ : 222, 270, 306, 519 nm [26];  $\text{Ph}_3\text{SnS}_2\text{CPh}$   $\lambda_{\text{max}}$ : 308, 315 nm [25];  $\text{Ph}_3\text{PbS}_2\text{CPh}$ ,  $\lambda_{\text{max}}$ : 222, 271, 303, 519 nm) [26]. In the latter derivatives the central metal atom adopts a distorted tetrahedral configuration with monodentate ligand moiety as shown by X-ray crystallography [26]. However, in mono- and di-phenyl tin and diphenyl lead derivatives, where ligands are asymmetrically chelated (by X-ray crystallography), thiocarbonyl transitions are blue shifted (e.g.,  $\text{Ph}_2\text{Sn}(\text{S}_2\text{Ctol-}o)_2$   $\lambda_{\text{max}}$ : 338, 457 nm,  $\text{Ph}_2\text{Pb}(\text{S}_2\text{CPh})_2$   $\lambda_{\text{max}}$ : 222, 272, 316, 472 nm) [26] owing to delocalization of electron density of the thiocarbonyl group ( $\text{C}=\text{S}$ ) into  $\text{S}=\text{C}=\text{S}$  linkage. The observed blue shifted absorption bands in the gallium and indium complexes suggest bidentate coordination of the dithiocarboxylate ligand. Absorption bands in the regions 1185–1265 and 710–725  $\text{cm}^{-1}$  in the IR spectra have been assigned to the  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}-\text{S})$  stretchings, respectively [25–27]. The spectra of organo-gallium and -indium complexes exhibited absorptions in the regions 575–595 and 510–520  $\text{cm}^{-1}$  for  $\nu(\text{Ga}-\text{C})$  and  $\nu(\text{In}-\text{C})$  stretchings, respectively [16c,17,28].

The mono- and di-methyl gallium/indium complexes displayed a singlet for  $\text{Me}-\text{M}$  group in their  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (Table 1). The signal is deshielded gradually on sequentially substituting a methyl group in  $\text{Me}_3\text{M}\cdot\text{OEt}_2$  by a dithio ligand thus provide a diagnostic tool ( $\sim-0.4$  ppm  $\text{Me}_3\text{M}\cdot\text{OEt}_2$ ;  $\sim 0.2$  ppm  $\text{Me}_2\text{M}(\widehat{\text{S}}\widehat{\text{S}})$ ;  $\sim 0.6$  ppm  $\text{MeM}(\widehat{\text{S}}\widehat{\text{S}})_2$ ). The thiocarbonyl ( $\text{CS}_2$ ) resonance in these complexes appears in the region 241–258 ppm and is considerably deshielded as compared to the corresponding resonance for the free ligands. We have investigated a series of classical and organo-gallium and -indium complexes with several dithiolate ligands,  $\text{XCS}_2$  ( $\text{X}=\text{R}_2\text{N}$ ,  $\text{RO}$ ,  $\text{R}$ ) [11,13,17,18]. The  $\text{CS}_2$  resonance showed pronounced dependence on  $\text{X}$  and is deshielded on moving from dithiocarbamate ( $\sim 201$  ppm), xanthate ( $\sim 228$  ppm) through dithiocarboxylate ( $\sim 250$  ppm). The  $^{13}\text{C}$  NMR shifts are sensitive to the nature (e.g., inductive effects) of the substituents and also to the energy of  $n-\pi^*$  transitions in carbonyl compounds [29]. The greater electron withdrawing property of the  $\text{OR}$  group than  $\text{NR}_2$  may be attributed to shielding of  $\text{CS}_2$  in dithiocarbamate complexes relative to xanthate derivatives. The observed  $\text{CS}_2$  shifts also reflect the energy trend of  $n-\pi^*$  transition in the thiocarbonyl group.

### 2.2. Structure of $[\text{MeGa}(\text{S}_2\text{Ctol})_2]$

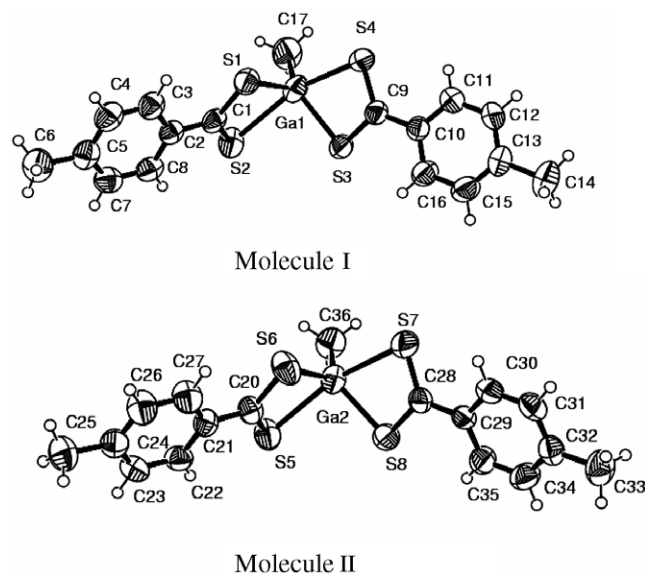
The molecular structure with crystallographic numbering scheme is shown in Fig. 1 and selected bond lengths and angles are summarized in Table 2. There are two crystallographically independent molecules within the same crystal. Gallium atom in each molecule adopts a geometry which is intermediate between trigonal bipyramidal and square pyramidal configurations as various angles around the central metal atom deviates significantly from the ideal values expected for the two configurations. The  $\text{C}-\text{Ga}-\text{S}$  angles in the two molecules vary between  $99.8(2)$  and  $130.9(2)^\circ$ . The two dithiocarboxylates in each molecule bind the gallium metal in an asymmetric chelating fashion and differ significantly from each other within a molecule. The two shorter  $\text{Ga}-\text{S}$  distances in each molecule are comparable (av.  $2.317 \text{ \AA}$ ) and are well within the single  $\text{Ga}-\text{S}$  bond [14,30]. However, this distance is smaller than the one reported for  $[[\text{Ga}\{\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2)_2\text{O}\}_3]$  (av.  $\text{Ga}-\text{S} = 2.438 \text{ \AA}$ ) [13],  $[\text{Ga}(\text{S}_2\text{CNEt}_2)_3]$  ( $2.465(2)$ ;  $2.405(2) \text{ \AA}$ ) [9a]. The sulfur atoms of shorter  $\text{Ga}-\text{S}$  distances have  $\text{S}-\text{Ga}-\text{S}$  angle of  $\sim 111^\circ$ . The two longer  $\text{Ga}-\text{S}$  distances in each molecule differ significantly  $2.6677(19)$ ,  $2.5165(18)$  for molecule-I; and  $2.6326(18)$ ,  $2.5571(18) \text{ \AA}$  for molecule-II which are longer than the sum of their covalent radii but smaller than the sum of their van der Waals radii. These sulfur atoms result into wider  $\text{S}-\text{Ga}-\text{S}$  angles of  $\sim 152.6^\circ$ .

There are distinctly two different types of  $\text{C}-\text{S}$  bonds (av.  $1.622$  and  $1.711 \text{ \AA}$ ) in molecule I. The shorter bond lengths are close to  $\text{C}=\text{S}$  distance whereas longer bond lengths are intermediate between their single and double bond carbon

Table 1  
Yield, m.p., analysis and  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data for gallium and indium dithiocarboxylates

Compound	Colour % (yield)	m.p. (°C)	% Ga/In Found (Calc)	UV–Vis $\lambda_{\text{max}}$ (nm)	IR in $\text{cm}^{-1}$			$^1\text{H}$ NMR data $\delta$ in ppm	$^{13}\text{C}\{^1\text{H}\}$ NMR data $\delta$ in ppm
					$\nu(\text{C}=\text{S})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{C})$		
PhCS <sub>2</sub> H	Red (67)	Liquid	–	304, 522	2365 (SH) 1170	722	–	6.40 (s, br, SH); 7.39 (br, 2H, H-3,5); 7.57 (br, 1H, H-4); 8.07 (br, 8.2 Hz, 2H, H-2,6).	126.7 (C-3,5); 128.2 (C-4); 133.0 (C-2,6); 143.5 (C-1); 225.2 (CS <sub>2</sub> )
[Me <sub>2</sub> Ga(S <sub>2</sub> CPh)]	Brown (98)	Liquid	27.3 (27.6)	317, 377 (sh)	1243, 1228	722	595	0.26 (s, Me <sub>2</sub> Ga); 7.37–7.44 (m, 2H, H-3,5); 7.61–7.64 (m, 1H, H-4); 8.33 (d, 7.3 Hz, 2H, H-2,6).	–2.5 (Me <sub>2</sub> Ga); 125.9 (C-3,5); 128.2 (C-4); 134.4 (C-2,6); 143.3 (C-1); 246.3 (CS <sub>2</sub> )
[MeGa(S <sub>2</sub> CPh) <sub>2</sub> ]	Brown (94)	Liquid	18.0 (17.8)	323, 462	1242, 1227	722	575	0.72 (s, MeGa); 7.40 (br, 2H, H-3,5); 7.62 (br, 1H, H-4); 8.35 (br, 2H, H-2,6).	0.46 (MeGa); 126.7 (C-3,5); 128.6 (C-4); 134.4 (C-2,6); 142.6 (C-1); 244.7 (CS <sub>2</sub> )
Ga(S <sub>2</sub> CPh) <sub>3</sub>	Yellow (82)	115	12.5 (13.2)	324, 407 (sh)	1245, 1225	722	–	7.44 (br, 2H, H-3,5); 7.66 (br, 1H, H-4); 8.40 (br, 2H, H-2,6)	127.0 (C-3,5); 128.3 (C-4); 134.4 (C-2,6); 141.7 (C-1); 243.7 (CS <sub>2</sub> ).
[Me <sub>2</sub> In(S <sub>2</sub> CPh)]	Brown (96)	Liquid	38.3 (38.5)	304, 367	1227	721	520	0.23 (s, Me <sub>2</sub> In); 7.40 (br, 2H, H-3,5); 7.69–7.60 (m, 1H, H-4); 8.35 (br, 2H, H-2,6)	–2.3 (Me <sub>2</sub> In); 127.9 (C-3,5); 129.0 (C-4); 132.3 (C-2,6); 248.1 (CS <sub>2</sub> ).
[MeIn(S <sub>2</sub> CPh) <sub>2</sub> ]	Brown (95)	Liquid	26.6 (26.3)	326, 464	1236, 1222	722	–	0.69 (s, MeIn); 7.42–7.36 (m, 2H, H-3,5); 7.64–7.59 (m, 1H, H-4); 8.41 (d, 7.5 Hz, 2H, H-2,6).	–1.9 (MeIn); 127.6 (C-3,5); 128.0 (C-4); 134.3 (C-2,6); 142.2 (C1); 245.7 (CS <sub>2</sub> ).
In(S <sub>2</sub> CPh) <sub>3</sub>	Yellow (83)	121	19.6 (19.9)	337, 423 (sh)	1221	722	–	7.35–7.47 (m, 2H, H-3,5); 7.60–7.66 (m 1H, H-4); 8.40 (br, 2H, H-2,6).	127.6 (C-3,5); 128.3 (C-4); 134.3 (C-2,6); 142.2 (C-1); 245.6 (CS <sub>2</sub> )
tolCS <sub>2</sub> H	Red (55)	98	–	529	1257, 1183	712	–	2.38 (s, Metol); 4.71 (s, SH); 7.19 (d, 8.3 Hz, 2H, H-3,5); 7.98 (d, 8.2 Hz, 2H, H-2,6) (C <sub>6</sub> H <sub>4</sub> )	21.5 (Me); 126.9 (C-2,6); 129.0 (C-3,5); 141.1 (C-4); 144.2 (C-1); 224.6 (CS <sub>2</sub> )
[Me <sub>2</sub> Ga(S <sub>2</sub> Ctol)]	Brown (96)	Semi solid	26.7 (26.1)	336	1248, 1227	723	595	0.25 (s, Me <sub>2</sub> Ga); 2.42 (Me-tol); 7.22 (d, 7.9 Hz, 2H, H-3,5); 8.24 (d, 8.1 Hz, 2H, H-2,6) (C <sub>6</sub> H <sub>4</sub> ).	–2.6 (Me <sub>2</sub> Ga); 21.7 (Me-tol); 126.1 (C-2,6); 128.9 (C-3,5); 141.1 (C-4); 145.9 (C-1); 245.2 (CS <sub>2</sub> )
[MeGa(S <sub>2</sub> Ctol) <sub>2</sub> ]	Orange (96)	110	15.9 (16.6)	345	1248, 1179	720	–	0.68 (s, MeGa); 2.41 (s, Me-tol); 7.20 (d, 7.9 Hz, 2H, H-3,5); 8.26 (d, 8.2 Hz, 2H, H-2,6) (C <sub>6</sub> H <sub>4</sub> ).	0.56 (MeGa); 21.6 (Me-tol); 126.9 (C-2,6); 128.8 (C-3,5); 140.5 (C-4); 145.8 (C-1); 243.6 (CS <sub>2</sub> ).
Ga(S <sub>2</sub> Ctol) <sub>3</sub>	Orange (92)	133	12.4 (12.2)	387, 443 (vw)	1249, 1180	724	–	2.42 (s, Me-tol); 7.20 (d, 8 Hz, C <sub>6</sub> H <sub>4</sub> ); 8.29 (d, 8 Hz) (C <sub>6</sub> H <sub>4</sub> ).	21.7 (s, Me-tol); 127.2 (C-2,6); 128.8 (C-3,5); 138.9 (C-4); 145.9 (C-1); 242.4 (CS <sub>2</sub> ).
[Me <sub>2</sub> In(S <sub>2</sub> Ctol)]	Yellow (97)	202 turns black	36.0 (36.8)	327	1245, 1224	721	510	0.26 (s, Me <sub>2</sub> In); 2.40 (Me-tol); 7.18 (d, 8.01 Hz, 2H, H-3,5); 8.25 (d, 7.9 Hz, 2H, H-2,6) (C <sub>6</sub> H <sub>4</sub> ).	–2.85 (s, Me <sub>2</sub> In); 21.6 (Me-tol); 127.0 (C-2,6); 128.6 (C-3,5); 143.2 (C-4); 145.3 (C-1); 241.2 (CS <sub>2</sub> )

In(S <sub>2</sub> Ctol) <sub>3</sub>	Orange (82)	148	18.5 (18.6)	349, 383, 440 (vw)	1244, 1180	722	–	2.41 (s, Me-tol); 7.18 (d, 9 Hz, 2H, H-3,5); 8.31 (d, 9 Hz, 2H, H-2,6) (C <sub>6</sub> H <sub>4</sub> ); 2.29 (s, 4-MeC <sub>6</sub> H <sub>2</sub> ); 2.38 (s, 2,6-MeC <sub>6</sub> H <sub>2</sub> ); 4.69 (SH); 6.87 (C <sub>6</sub> H <sub>2</sub> )
MesCS <sub>2</sub> H	Red (55)	Liquid		420 516		721	–	19.1 (2,6-MeC <sub>6</sub> H <sub>2</sub> ); 20.8 (4-MeC <sub>6</sub> H <sub>2</sub> ); 128.6 (C-3,5); 131.2 (C-4); 138.1 (C-2,6); 146.4 (C-1); 235.7 (CS <sub>2</sub> )
Ga(S <sub>2</sub> CMes) <sub>3</sub>	Orange (93)	197	10.3 (10.6)	337, 423	1264, 1242	722	–	19.4 (2,6-MeC <sub>6</sub> H <sub>2</sub> ); 21.04 (4-MeC <sub>6</sub> H <sub>2</sub> ); 128.6 (C-3,5); 132.3 (C-4); 138.3 (C-2,6); 142.4 (C-1); 255.7 (CS <sub>2</sub> )
In(S <sub>2</sub> CMes) <sub>3</sub>	Yellow (91)	217	16.4 (16.4)	347, 442	1260, 1235	725	–	19.4 (2,6-MeC <sub>6</sub> H <sub>2</sub> ); 20.9 (4-MeC <sub>6</sub> H <sub>2</sub> ); 128.6 (C-3,5); 131.3 (C-4); 138.0 (C-2,6); 143.45 (C-1); 258.3 (CS <sub>2</sub> )

Fig. 1. ORTEP of [MeGa(S<sub>2</sub>Ctol)<sub>2</sub>] with atomic numbering scheme.Table 2  
Selected bond distances (Å) and bond angles (deg) of [MeGa(S<sub>2</sub>Ctol)<sub>2</sub>]

Molecule I		Molecule II	
Ga(1)–C(17)	1.936 (6)	Ga(2)–C(36)	1.941 (6)
Ga(1)–S(1)	2.3176 (17)	Ga(2)–S(5)	2.5571 (18)
Ga(1)–S(2)	2.6677 (19)	Ga(2)–S(6)	2.3111 (18)
Ga(1)–S(3)	2.3188 (16)	Ga(2)–S(7)	2.6326 (18)
Ga(1)–S(4)	2.5165 (18)	Ga(2)–S(8)	2.3209 (17)
C(1)–S(1)	1.719 (5)	C(20)–S(5)	1.683 (5)
C(1)–S(2)	1.667 (5)	C(20)–S(6)	1.704 (5)
C(9)–S(3)	1.703 (5)	C(28)–S(7)	1.677 (5)
C(9)–S(4)	1.678 (5)	C(28)–S(8)	1.702 (5)
C(1)–C(2)	1.481 (7)	C(20)–C(21)	1.469 (7)
C(9)–C(10)	1.461 (7)	C(28)–C(29)	1.462 (7)
C(17)–Ga(1)–S(2)	99.8 (2)	C(36)–Ga(2)–S(7)	103.41 (19)
C(17)–Ga(1)–S(3)	130.9 (2)	C(36)–Ga(2)–S(6)	123.96 (19)
C(17)–Ga(1)–S(4)	106.1 (2)	C(36)–Ga(2)–S(8)	124.61 (19)
C(17)–Ga(1)–S(1)	117.7 (2)	C(36)–Ga(2)–S(5)	105.36 (19)
S(1)–Ga(1)–S(2)	71.05 (5)	S(5)–Ga(2)–S(6)	72.63 (6)
S(1)–Ga(1)–S(3)	110.94 (6)	S(5)–Ga(2)–S(7)	151.20 (7)
S(1)–Ga(1)–S(4)	96.95 (6)	S(5)–Ga(2)–S(8)	93.03 (6)
S(2)–Ga(1)–S(3)	89.37 (6)	S(6)–Ga(2)–S(7)	90.13 (7)
S(2)–Ga(1)–S(4)	154.06 (6)	S(6)–Ga(2)–S(8)	111.33 (7)
S(3)–Ga(1)–S(4)	73.14 (5)	S(7)–Ga(2)–S(8)	71.51 (5)
Ga(1)–S(1)–C(1)	90.27 (18)	Ga(2)–S(5)–C(20)	81.39 (18)
Ga(1)–S(2)–C(1)	80.08 (19)	Ga(2)–S(6)–C(20)	88.84 (18)
S(1)–C(1)–S(2)	118.6 (3)	S(5)–C(20)–S(6)	117.1 (3)
S(1)–C(1)–C(2)	119.0 (4)	S(5)–C(20)–C(21)	121.9 (4)
S(2)–C(1)–C(2)	112.5 (4)	S(6)–C(20)–C(21)	120.9 (4)
Ga(1)–S(3)–C(9)	87.75 (17)	Ga(2)–S(7)–C(28)	80.06 (18)
Ga(1)–S(4)–C(9)	81.96 (18)	Ga(2)–S(8)–C(28)	89.52 (18)
S(3)–C(9)–S(4)	117.1 (3)	S(7)–C(28)–S(8)	118.6 (3)
S(3)–C(9)–C(10)	121.3 (4)	S(7)–C(28)–C(29)	121.5 (4)
S(4)–C(9)–C(10)	121.6 (4)	S(8)–C(28)–C(29)	119.9 (4)

sulfur distances [25,31]. In molecule **II** all the four C–S distances, however, have nearly same values (varying between 1.677(5) and 1.704(5) Å) and lie between the single and double bond carbon–sulfur distances [25,31].

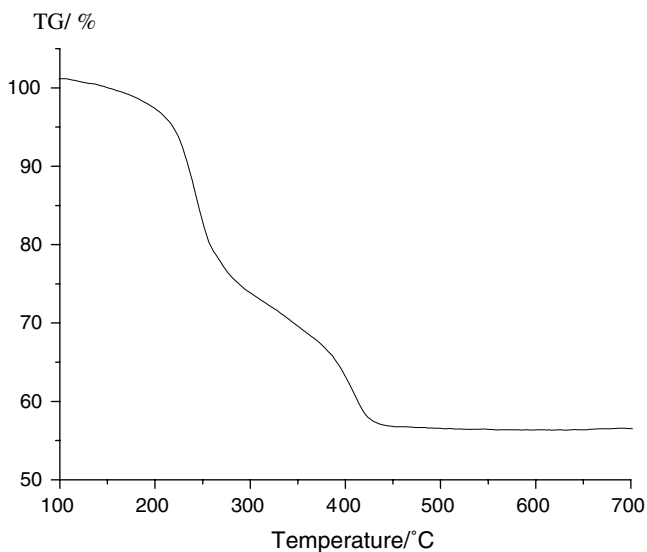


Fig. 2. TG curve of  $[\text{Me}_2\text{In}(\text{S}_2\text{Ctol})]$ .

### 3. Experimental

All experiments involving organogallium/indium compounds were performed under anhydrous conditions in a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard procedures. Anhydrous indium trichloride was used as such. The ether adduct of  $\text{Me}_3\text{In}$  was prepared from  $\text{MeMgI}$  and indium trichloride whereas ether adduct of trimethyl gallium was prepared from gallium magnesium alloy and methyl iodide. Dithiocarboxylic acids were prepared by the reported methods [32]. Infrared spectra were recorded as neat liquids or as Nujol mulls between CsI plates on a Bomem MB-102 FT IR spectrometer. The NMR spectra ( $^1\text{H}$ , and  $^{13}\text{C}\{^1\text{H}\}$ ) were recorded on a Bruker DPX-300 NMR spectrometer in 5 mm tube in  $\text{CDCl}_3$  solution. Chemical shifts were referenced to the internal chloroform peak ( $\delta$  7.26 and  $\delta$  77.0 ppm) for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ , respectively. Electronic spectra were recorded in benzene on a Chemito Spectrascan UV double beam UV-vis spectrophotometer. The TG analysis of  $[\text{Me}_2\text{InS}_2\text{Ctol}]$  was performed on a Netzsch STA PC Luxx instrument which was calibrated with  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . Powder X-ray diffraction data were collected on a Philips PW 1820.

#### 3.1. $[\text{MeGa}(\text{S}_2\text{Ctol})_2]$

To a benzene solution ( $25 \text{ cm}^3$ ) of trimethylgallium etherate (431 mg, containing 187 mg  $\text{Me}_3\text{Ga}$ , 1.6 mmol), a solution of  $\text{tolCS}_2\text{H}$  (551 mg, 3.2 mmol) in the same solvent was added and the whole was stirred under a nitrogen atmosphere for 4 h. The solvent was stripped off under reduced pressure leaving behind an orange solid which was then crystallized with dichloromethane/hexane (Yield: 662 mg, 96%). Similarly, all other mono methyl indium/gallium complexes were prepared.

#### 3.2. $[\text{Me}_2\text{Ga}(\text{S}_2\text{Ctol})]$

To a benzene solution ( $25 \text{ cm}^3$ ) of trimethylgallium etherate (510 mg, containing 222 mg  $\text{Me}_3\text{Ga}$ , 1.9 mmol), a solution of  $\text{tolCS}_2\text{H}$  (326 mg, 1.9 mmol) in the same solvent was added and stirred under nitrogen atmosphere for 4 h. The solvent was stripped off under reduced pressure leaving behind an orange viscous liquid, which turns semi solid after few days (Yield: 500 mg, 96%). Similarly, all other dimethyl indium/gallium complexes were prepared.

#### 3.3. $\text{In}(\text{S}_2\text{CPh})_3$

To a benzene suspension of  $\text{InCl}_3$  (25 ml) (654 mg, 2.9 mol), a benzene solution of  $\text{PhCS}_2\text{H}$  (25 ml) (1.366 g, 8.8 mmol) was added followed by the addition of  $\text{Et}_3\text{N}$  (896 mg, 8.8 mmol). The solution was then stirred for 3 h and filtered through a G-3 filtration unit. Benzene was removed from the filtrate *in vacuo* to give a yellow solid which was then crystallized from benzene hexane mixture (Yield: 1.409 g, 83%). Similarly other tris complexes were

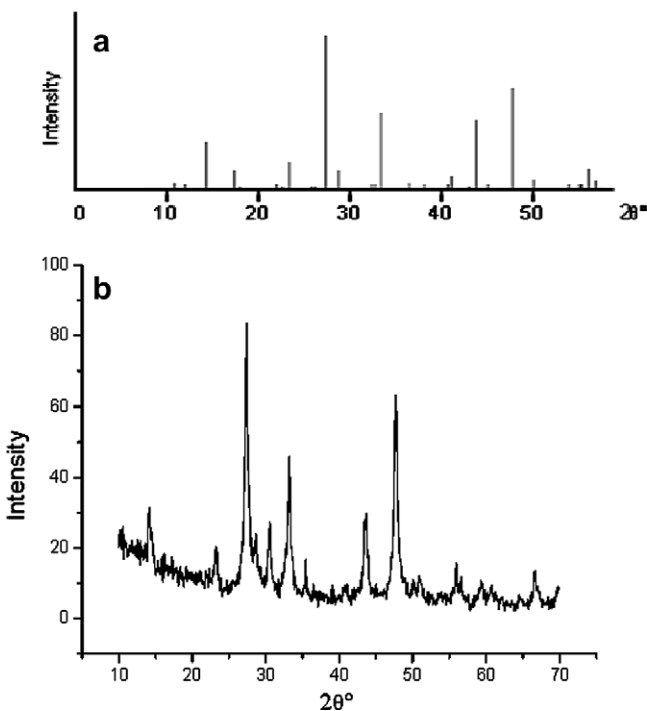


Fig. 3. XRD pattern of  $\beta\text{-In}_2\text{S}_3$ : (a) standard file JCPDS No: 25-0390 and (b) obtained from pyrolysis of  $[\text{Me}_2\text{In}(\text{S}_2\text{Ctol})]$  at  $600^\circ\text{C}$ .

#### 2.3. Thermal behavior

TG curve of  $\text{Me}_2\text{In}(\text{S}_2\text{Ctol})$  showed a two-step decomposition with the onset temperatures  $222$  and  $390^\circ\text{C}$  with the formation of tetragonal  $\beta\text{-In}_2\text{S}_3$  from weight loss (found: 44.7%; calcd: 47.7%) (Fig. 2) and XRD pattern (JCPDS File No. 25-0390). On further heating in the range  $600\text{--}1000^\circ\text{C}$ , there is an additional weight loss leading to the formation  $\text{In}_6\text{S}_7$  (from XRD pattern; JCPDS File No. 190587). Furnace heating of this complex at  $600^\circ\text{C}$  under flowing  $\text{N}_2$  also gave tetragonal  $\beta\text{-In}_2\text{S}_3$  (Fig. 3).

Table 3  
Crystallographic and structural refinement data of [MeGa(S<sub>2</sub>Ctol)<sub>2</sub>]

Formula	C <sub>17</sub> H <sub>17</sub> GaS <sub>4</sub>
Formula weight	419.27
Crystal size (mm <sup>3</sup> )	0.45 × 0.32 × 0.19
Temperature (K)	293 (2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Cell	
<i>a</i> (Å)	6.1187 (19)
<i>b</i> (Å)	32.596 (10)
<i>c</i> (Å)	19.038 (6)
β (°)	90.111(6)
<i>V</i> (Å <sup>3</sup> )/ <i>Z</i>	3797(2)/4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.467
μ (mm <sup>-1</sup> )/ <i>F</i> (000)	1.882/1712
Limiting indices	-8 ≤ <i>h</i> ≤ 7; -41 ≤ <i>k</i> ≤ 43; -25 ≤ <i>l</i> ≤ 25
Number of reflections collect/unique	32695/9024
<i>R</i> <sub>int</sub>	0.0480
Number of data/restrictions/parameters	9024/0/403
Goodness of fit on <i>F</i> <sup>2</sup>	0.983
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices [ <i>I</i> > 2σ ( <i>I</i> )]	0.1678; 0.0659
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1789; 0.1394

prepared. In some preparations complexes were contaminated by Et<sub>3</sub>N · HCl which could be removed by washing with dry methanol and finally drying the complex under vacuum.

### 3.4. X-ray crystallographic study of [MeGa(S<sub>2</sub>Ctol)<sub>2</sub>]

The unit cell parameters and intensity data for single crystal of [MeGa(S<sub>2</sub>Ctol)<sub>2</sub>] were collected at 293(2) K on a Bruker Smart APEX CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å), employing the ω scan technique. The intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved and refined with SHELX program [33]. The non-hydrogen atoms were refined anisotropically. Crystallographic data are given in Table 3.

## 4. Supplementary materials

CCDC 293633 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## Acknowledgements

One of the authors (SG) is grateful for the award of a Senior Research Fellowship by the Department of Atomic Energy. Authors thank Drs. T. Mukherjee and S.K. Kulshreshtha for encouragement of this work.

## References

- [1] K.A. Evans, in: A.J. Downs (Ed.), Chemistry of Aluminium, Gallium, Indium and Thallium, Blackie, London, 1993.
- [2] S. Schulz, E.G. Gillan, J.L. Ross, L.M. Rogers, R.D. Rogers, A.R. Barron, Organometallics 15 (1996) 4880.
- [3] A.R. Barron, Adv. Mater. Opt. Electron 5 (1995) 245.
- [4] S.W. Haggata, M.A. Mallik, M. Motevalli, P. O'Brien, Chem. Mater. 7 (1995) 716.
- [5] M. Lazell, P. O'Brien, J.D. Otway, J. Park, J. Chem. Soc. Dalton Trans. (2000) 4479.
- [6] (a) R. Nomura, S.J. Inazawa, K. Kanaya, H. Matsuda, Appl. Organomet. Chem. 3 (1989) 195;  
(b) R. Nomura, S. Fujii, K. Kanaya, H. Matsuda, Polyhedron 9 (1990) 361;  
(c) R. Nomura, K. Konishi, H.J. Matsuda, J. Electrochem. Soc. 138 (1991) 631;  
(d) R. Nomura, K. Konishi, H. Matsuda, Thin Solid Films 198 (1991) 339;  
(e) M.B. Power, A.R. Barron, J. Chem. Soc. Chem. Commun. (1991) 1315;  
(f) M.B. Power, J.W. Ziller, A.N. Tyler, A.R. Barron, Organometallics 11 (1992) 1055;  
(g) A.N. MacInnes, W.M. Cleaver, A.R. Barron, M.B. Power, A.F. Hepp, Adv. Mater. Opt. Electron. 1 (1992) 229;  
(h) A.N. MacInnes, M.B. Power, A.F. Hepp, A.R. Barron, J. Organomet. Chem. 449 (1993) 95;  
(i) S.L. Stoll, S.G. Bott, A.R. Barron, J. Chem. Soc., Dalton Trans (1997) 1315.
- [7] C.C. Landry, A. Hynes, A.R. Barron, I. Haiduc, C. Silvestru, Polyhedron 15 (1996) 391.
- [8] G. Shang, K. Kunze, M.J. Hampden-Smith, E.N. Duesler, Adv. Mater., Chem. Vap. Deposition 2 (1996) 242.
- [9] (a) B.F. Hoskins, E.R.T. Tiekink, R. Vecchiet, G. Winter, Inorg. Chim. Acta. 90 (1984) 197;  
(b) F. Galsbol, C.E. Schaffer, Inorg. Synth. 10 (1967) 42;  
(c) S. Abram, U. Abram, Inorg. Chim. Acta 153 (1988) 135.
- [10] V.G. Bessdergenev, E.N. Ivanova, Y.A. Kovalevskaya, S.A. Gromilov, V.N. Kirichenko, S.V. Larionov, Inorg. Mater. 32 (1996) 592.
- [11] D.P. Dutta, G. Sharma, S. Ghoshal, N.P. Kushwah, V.K. Jain, J. Nanosci. Nanotech. 6 (2006) 235.
- [12] (a) S.W. Haggata, M.A. Mallik, M. Motevalli, P. O'Brien, J. Organomet. Chem. 511 (1996) 199;  
(b) P. O'Brien, D.J. Otway, J.R. Walsh, Thin Solid Films 315 (1998) 57;  
(c) D.P. Dutta, V.K. Jain, E.R.T. Tiekink, Main Group Metal Chem. 21 (1998) 293.
- [13] D.P. Dutta, V.K. Jain, A. Knoedler, W. Kaim, Polyhedron 21 (2002) 239.
- [14] J. Park, P. O'Brien, A.J.P. White, D.J. Williams, Inorg. Chem. 40 (2001) 3629.
- [15] (a) M. Weiber, T. Clarius, Phosh. Sulf. Silicon Related Elem. 102 (1995) 261;  
(b) G.E. Coates, R.N. Mukherjee, J. Chem. Soc. (1964) 1295.
- [16] (a) D. Pahari, V.K. Jain, Main Group Met. Chem. 20 (1997) 691;  
(b) D. Pahari, V.K. Jain, R.P. Patel, Main Group Met. Chem. 21 (1998) 261;  
(c) N. Prasad, D.P. Dutta, V.K. Jain, Main Group Met. Chem. 25 (2002) 677.
- [17] S. Ghoshal, N.P. Kushwah, D.P. Dutta, V.K. Jain, Appl. Organomet. Chem. 19 (2005) 1257.
- [18] D.P. Dutta, V.K. Jain, S. Chaudhury, E.R.T. Tiekink, Main Group Metal Chem. 24 (2001) 405.
- [19] M. Afzaal, M.A. Malik, P. O'Brien, Chem. Commun. (2004) 334.
- [20] T. Maeda, R. Okawara, J. Organomet. Chem. 39 (1972) 87.
- [21] N. Kano, T. Kawashima, Top. Curr. Chem. 251 (2005) 141.
- [22] C. Furlani, M.L. Luciani, Inorg. Chem. 7 (1968) 1586.
- [23] S. Kato, M. Mizuta, Bull. Chem. Soc. Jap. 45 (1972) 3492.
- [24] P. Beslin, A. Dlubala, G. Levesque, Synthesis (1987) 835.

- [25] V. Coldea, I. Haiduc, *Synth. React. Inorg. Met. Org. Chem.* 10(1980) 417.
- [26] S. Kato, K. Tani, N. Kitaoka, K. Yamada, H. Mifune, *J. Organomet. Chem.* 611 (2000) 190.
- [27] S. Kato, Y. Itoh, Y. Ohta, K. Goto, M. Kimura, M. Mizuta, T. Murai, *Chem. Ber.* 118 (1985) 1696.
- [28] J. Weidlein, *Z. Anorg. Allg. Chem.* 386 (1971) 129.
- [29] C.H. Yoder, C.D. Schaeffer Jr., *Introduction to Multinuclear NMR: Theory and Application*, The Benjamin Cummings Publishing Company, Inc., Menlo Park, 1987.
- [30] S. Bhattacharya, N. Seth, D.K. Srivastava, V.D. Gupta, H. Noeth, M.T. Homann-Albach, *J. Chem. Soc., Dalton Trans.* (1996) 2815.
- [31] Covalent bond radii, C–S = 1.81 Å; C=S = 1.61 Å.
- [32] R.W. Bost, W.J. Mattox, *J. Am. Chem. Soc.* 52 (1930) 332; P. Beslin, A. Dlubala, G. Levesue, *Synthesis* (1987) 835.
- [33] G.M. Sheldrick, *SHELX-97*, A computer program for crystal structure solution and refinement, Universitaet Gottingen, Gottingen, Germany, 1997.