

## Tris(dithiocarboxylato)indium(III): Thermal studies and crystal structure of [In(S<sub>2</sub>Ctol)<sub>3</sub>]

SHAMIK GHOSHAL<sup>a</sup>, NISHA P KUSHWAH<sup>a</sup>, MANOJ K PAL<sup>a</sup>, VIMAL K JAIN<sup>a,\*</sup> and MUNIRATHINAM NETHAJI<sup>b</sup>

<sup>a</sup>Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085

<sup>b</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012  
e-mail: jainvk@barc.gov.in

MS received 20 October 2007; revised 15 March 2008

**Abstract.** Tris(dithiocarboxylato)indium(III), [In{S<sub>2</sub>CAr}<sub>3</sub>] (Ar = phenyl or *p*-tolyl) have been synthesized and characterized. The molecular structure of [In(S<sub>2</sub>Ctol)<sub>3</sub>] established by single crystal X-ray diffraction revealed a distorted octahedral geometry with symmetrically chelating dithiocarboxylate groups. These complexes on thermolysis gave β-In<sub>2</sub>S<sub>3</sub> which was characterized by XRD and EDX.

**Keywords.** Indium; dithiocarboxylate; crystal structure; β-In<sub>2</sub>S<sub>3</sub>.

### 1. Introduction

Classical and organometallic chemistry of gallium and indium with 1,1-dithiolate ligands (scheme 1) has been investigated for more than half a century and in general ligands of types A–C have been used in these studies.<sup>1</sup> The potential of these complexes as a single source precursor for the preparation of metal sulfide thin films and nanoparticles has been realized only recently.<sup>1–4</sup> Indium sulfide (β-In<sub>2</sub>S<sub>3</sub>), a direct band semiconductor, finds applications in opto-electronic and photovoltaic devices and as passivating agents for III-V devices.

Recently we have reported dithiocarboxylates of gallium and indium.<sup>5</sup> Dimethylindium dithiocarboxylates on thermolysis afforded β-In<sub>2</sub>S<sub>3</sub>.<sup>5</sup> The present work has been carried out with the objective to identify structural motif adopted by tris dithiocarboxylate complexes and to assess their suitability as molecular precursors for the preparation of indium sulfide nanoparticles. The results of this work are reported here.

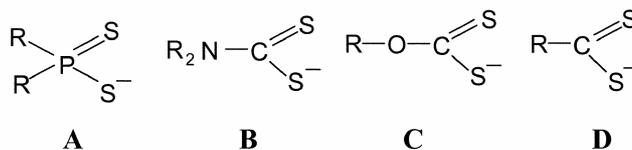
### 2. Experimental

#### 2.1 Materials and methods

All experiments involving indium compounds were performed under anhydrous conditions in a nitrogen

atmosphere using Schlenk techniques. Solvents were dried by standard procedure. Anhydrous indium trichloride was used as such. Dithiocarboxylic acids were prepared by the reported methods.<sup>6</sup> Infrared spectra were recorded between CsI plates on a Bomem MB-102 FT IR spectrophotometer. NMR spectra (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) were recorded on a Bruker DPX – 300 MHz instrument in 5 mm tubes in CDCl<sub>3</sub> solution. Chemical shift were referenced to the internal chloroform peak (δ 7.26 and δ 77.0 ppm for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}, respectively). The TG analysis was performed on a Netzsch STA PC Luxx instrument, which was calibrated with CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O. Powder X-ray diffraction data were collected on a Philips PW 1820. Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time of flight mass spectrometer. EDX experiments were carried out on a Kevex Instrument and SEM was recorded on Tescan Vega 2300T/40 instrument.

The complexes [In(S<sub>2</sub>CPh)<sub>3</sub>] (Mp: 121°C, IR: 1244, 1221 ν(C=S), 722 ν(C–S). UV-Vis: 337, 423 (sh). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.35–7.47 (*m*, 2H, H3, 5);



Scheme 1.

\*For correspondence

**Table 1.** Crystallographic and structural refinement data of  $[\text{In}(\text{S}_2\text{Ctol})_3]\cdot\text{C}_6\text{H}_6$ .

Formula	$\text{C}_{30}\text{H}_{27}\text{InS}_6$
Formula weight	694.70
Crystal size (mm)	$0.35 \times 0.28 \times 0.22$
$T$ (K)	273 (2)
Crystal system	Monoclinic
Space group	$C2/c$
$a$ (Å)	16.939 (6)
$b$ (Å)	15.814 (5)
$c$ (Å)	11.955 (4)
$\beta$ (°)	97.435 (6)
$V$ (Å <sup>3</sup> )	3175.5 (18)
$Z$	4
$d_{\text{cal}}$ (g cm <sup>-3</sup> )	1.453
$\mu$ (mm <sup>-1</sup> )/ $F(000)$	1.157/1408
Limiting indices	$-22 \leq h \leq 20$ ; $-20 \leq k \leq 18$ ; $-15 \leq l \leq 15$
Number of reflections/unique reflections	13500/3727
Number of data/restraints/parameters	3727/0/171
Final $R_1$ [ $I > 2\sigma(I)$ ]	0.0444, 0.1751
$R_1, WR_2$ (all data)	0.0758, 0.2241
Goodness of fit on $F^2$	0.812

7.60–7.66 (*m*, 1H, H4) 8.40 (*br*, 2H, H 2,6) <sup>13</sup>C{<sup>1</sup>H} NMR: 127.6 (C3, 5); 128.3 (C4); 134.3 (C2,6); 142.2 (C1); 245.6 (CS<sub>2</sub>). Mass spectra: 421 (M–L); 192 ([M–L<sub>2</sub>–CS<sub>2</sub>]); 121 (Ph CS<sub>2</sub>–S)) and [In(S<sub>2</sub>Ctol)<sub>3</sub>] (Mp: 148°C, IR: 1244, 1180  $\nu$ (C=S), 722  $\nu$ (C–S). UV–Vis: 349, 383, 440 (*vw*). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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>) <sup>13</sup>C{<sup>1</sup>H} NMR: 21.7 (Me–tol); 127.9 (C-2, 6); 128.6 (C3, 5); 140.0 (C4); 145.8 (C1); 244.5 (CS<sub>2</sub>). Mass spectra: 449 (M–L); 373 ([M–L]–CS<sub>2</sub>); 135 (tol CS<sub>2</sub>–S); 102 (tol CS<sub>2</sub>–S<sub>2</sub>); 91 (MeC<sub>6</sub>H<sub>4</sub>) were prepared according to literature method.<sup>5</sup>

## 2.2 Preparation of $\beta\text{-In}_2\text{S}_3$ nanoparticles

In a typical experiment [In(S<sub>2</sub>CAr)<sub>3</sub>] (Ar = Ph, tol) (100 mg) was taken in a round bottom flask fitted with a Liebig condenser under N<sub>2</sub>. Hexadecylamine (10 g) was added and this mixture was refluxed (330°C) with stirring for 4 h. The greenish-yellow residue obtained after decomposition was washed thoroughly with methanol and dried *in vacuo*.

## 2.3 Crystallography

Intensity data for single crystal of [In(S<sub>2</sub>Ctol)<sub>3</sub>] were collected on a Bruker Smart APEX CCD diffractometer using Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å), employing the  $\omega$  scan technique. The intensity data were

corrected for Lorentz, polarization and absorption effects. The structure was solved and refined with SHELEX program.<sup>7</sup> The non-hydrogen atoms were refined anisotropically. Crystallographic data are given in table 1 and are deposited to CCDC (No 680806).

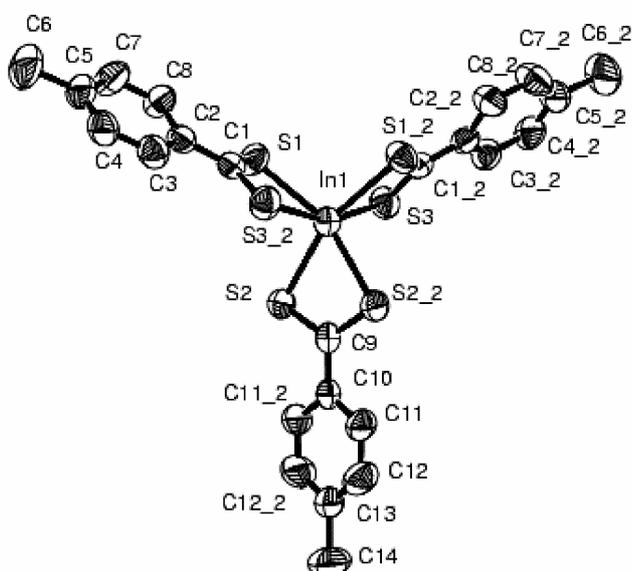
## 3. Results and discussion

The complexes, [In(S<sub>2</sub>CAr)<sub>3</sub>] (Ar = Ph or tol) have been synthesized by the reaction of InCl<sub>3</sub> with an appropriate dithiocarboxylic acid in the presence of triethylamine as HCl scavenger.<sup>5</sup> The resulting complexes were recrystallised from benzene-hexane as yellow orange crystalline solids which gave satisfactory analysis. Their NMR data (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) were in conformity with the reported values. The mass spectra of these complexes did not show molecular ion peaks, but displayed peaks attributable to ‘M–L’ fragment ( $m/z = 421$  (Ar = Ph); and 449 (Ar = tol)).

The structure of [In(S<sub>2</sub>Ctol)<sub>3</sub>] has been established unambiguously by single crystal X-ray diffraction analysis. The complex crystallizes with a molecule of benzene which is omitted from figure 1. Selected bond lengths and angles are given in table 2. The indium atom adopts a trigonally distorted octahedral geometry. All the three dithiocarboxylate ligands are symmetrically chelated to indium atom with very similar all the six In–S distances (av. 2.06 Å) which

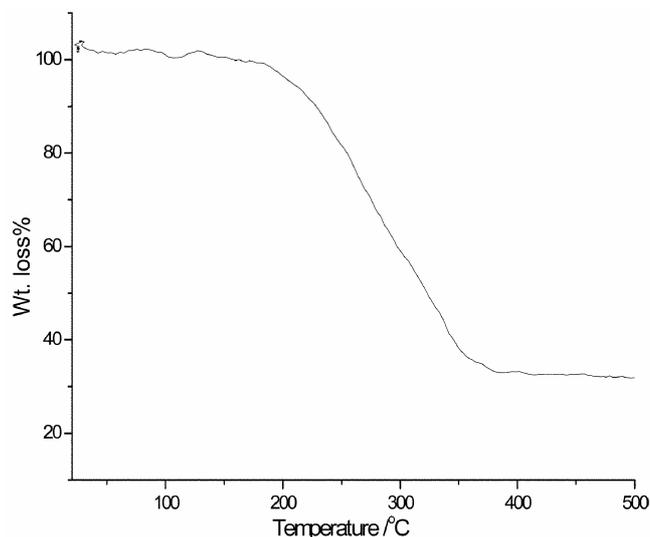
**Table 2.** Selected bond distances (Å) and bond angles (deg) of  $[\text{In}(\text{S}_2\text{Ctol})_3]\cdot\text{C}_6\text{H}_6$ .

In1-S1	2.5900 (14)	C1-S1	1.698 (5)
In1-S1_2	2.5900 (14)	C1-S3_2	1.690 (5)
In1-S2	2.6077 (14)	C9-S2	1.695 (3)
In1-S2_2	2.6077 (14)	C9-S2_2	1.695 (3)
In1-S3	2.6104 (16)	C1_2-S3	1.690 (5)
In1-S3_2	2.6104 (16)	C1-C2	1.469 (7)
S1-In1-S2	96.21 (5)	S1-In1-S3	97.18 (4)
S1-In1-S2_2	160.06 (5)	S2-In1-S3	100.12 (5)
S1_2-In1-S2_2	96.21 (5)	S2-In1-S3_2	97.79 (5)
S1_2-In1-S2	160.06 (5)	C9-S2-In1	86.3 (2)
S1_2-In1-S3_2	97.18 (4)	C1_2-S3-In1	85.30 (15)
S1-In1-S3_2	68.73 (4)	C1-S1-In1	85.81 (15)
S2_2-In1-S3	97.79 (5)	S3-C1-S1_2	120.1 (3)
S2_2-In1-S3_2	100.12 (5)	S2-C1-S2_2	119.2 (4)

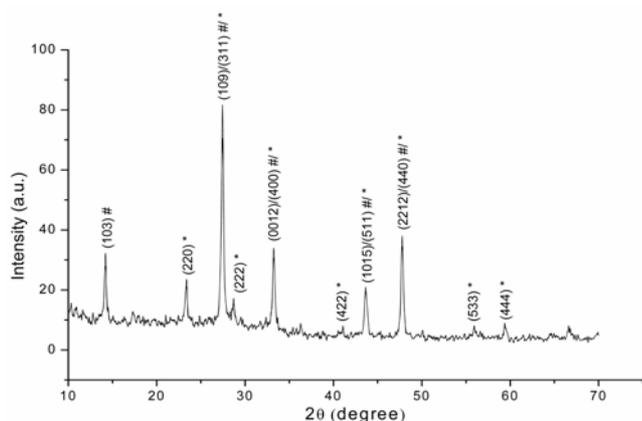
**Figure 1.** Molecular structure of  $[\text{In}\{\text{S}_2\text{Ctol}\}_3]$ . Hydrogen atoms are omitted for clarity.

agree well with the reported values.<sup>8-10</sup> The two C-S distances (av. 1.69 Å) are also similar as a consequence of symmetrical chelation of the dithiocarboxylate ligand, indicating delocalization in 'CS<sub>2</sub>' skeleton. The four-membered 'InS<sub>2</sub>C' rings are planar. The S-In-S angle (68.73°) is as expected for a small bite dithio ligand. The S-In-S angles<sup>1</sup> for tris (xanthato/dithiocarbamate)indium(III) are ~69°.

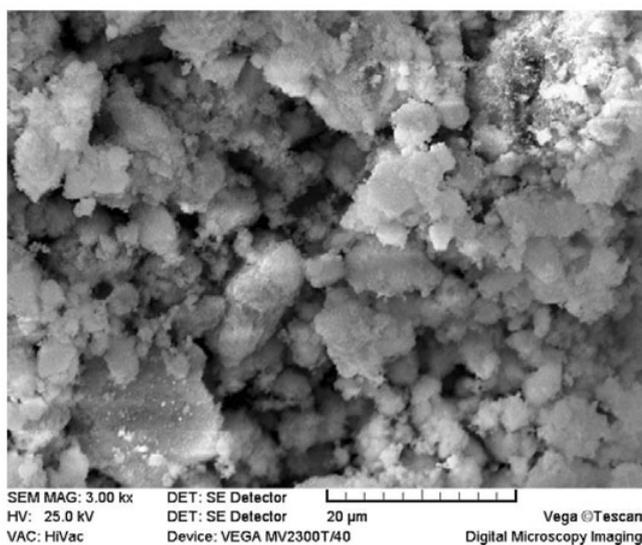
We have recently reported structures of  $\text{Sb}(\text{S}_2\text{Ctol})_3$  and  $\text{Bi}(\text{S}_2\text{CPh})_3$  in which dithiocarboxylate ligands are asymmetrically chelated with the M-S distance differing by 0.17–0.45 and 0.12–0.36 Å, respectively.<sup>11</sup> In these complexes metal atoms acquire a pyramidal configuration with stereochemically active lone pair of electrons.<sup>11</sup>

**Figure 2.** TG curve of  $\text{In}\{\text{S}_2\text{CPh}\}_3$ .

Decomposition of  $[\text{In}(\text{S}_2\text{CPh})_3]$  was studied by thermogravimetric analysis (TGA) (figure 2) which showed a single step of decomposition with the onset temperature of 190°C and weight loss of 69.8% (Calcd wt loss 71.6% for  $\text{In}_2\text{S}_3$ ). Pyrolysis of these complexes was carried out in various solvents such as ethylene glycol (190°C), 1,4-butane diol (230°C), polyethylene glycol (290°C) and hexadecylamine (HDA) (330°C). Thermolysis in glycols gave products showing very broad XRD patterns. Pyrolysis in HDA at 330°C, however, proceeded cleanly with the formation of  $\beta\text{-In}_2\text{S}_3$ . The X-ray diffraction pattern (XRD) of the later indicated predominance of tetragonal phase (JCPDS File No: 25-0390) (figure 3) with some contamination of cubic phase (JCPDS



**Figure 3.** XRD pattern of  $\beta$ - $\text{In}_2\text{S}_3$  (# Tetragonal, \*Cubic) obtained from thermolysis of  $[\text{In}\{\text{S}_2\text{CPh}\}_3]$  in HDA.



**Figure 4.** SEM micrograph of  $\beta$ - $\text{In}_2\text{S}_3$  obtained from thermolysis of  $[\text{In}(\text{S}_2\text{CPh})_3]$  in refluxing HDA.

File No: 32-0456). Energy dispersive X-ray analysis (EDX) of these samples were consistent with  $\text{In}_2\text{S}_3$  (Found: In = 70.1%, S = 29.9% (from  $[\text{In}(\text{S}_2\text{CPh})_3]$ ); In = 69.4%, S = 30.6% (from  $[\text{In}(\text{S}_2\text{Ctol})_3]$ ) and Calcd for  $\text{In}_2\text{S}_3$ : In = 70.5%; S = 29.5%). The scanning electron microscopy (SEM) images (figure 4) of these particles revealed their spherical nature.

### Acknowledgement

The authors thank Drs D Das and T Mukherjee for their encouragement.

### References

1. Ghoshal S and Jain V K 2007 *J. Chem. Sci.* **119** 583
2. Afzal M, Malik M A and O'Brien P 2004 *Chem. Commun.* 334
3. Ghoshal S, Kushwah N P, Dutta D P and Jain V K 2005 *Appl. Organomet. Chem.* **19** 1257
4. Dutta D P, Sharma G, Ghoshal S, Kushwah N P and Jain V K 2006 *J. Nanosci. Nanotech.* **6** 235
5. Ghoshal S, Jain V K, Dutta D P, Phadnis P P and Nethaji M 2006 *J. Organomet. Chem.* **691** 5838
6. Bost R W and Mattox W J 1930 *J. Am. Chem. Soc.* **52** 332; Beslin P, Dlubala A and Levesue G 1987 *Synthesis* 835
7. Sheldrick G M 1997 SHELX-97, A computer program for crystal structure solution and refinement, Universitaet Gottingen, Gottingen, Germany
8. Dutta D P, Jain V K, Knoedler A and Kaim W 2002 *Polyhedron* **21** 239
9. Zuckerman-Schpector J, Haiduc I, Silvestru C and Cea-Olivares R 1995 *Polyhedron* **14** 3094
10. Svensson G and Albertsson J 1989 *Acta Chem. Scand.* **43** 511
11. Chaudhary K P, Wadawale A P, Ghoshal S, Chopade S M, Sagoria V S and Jain V K unpublished results.