Gallium(III) and indium(III) dithiolate complexes: Versatile precursors for metal sulfides

SHAMIK GHOSHAL and VIMAL K JAIN*

Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085
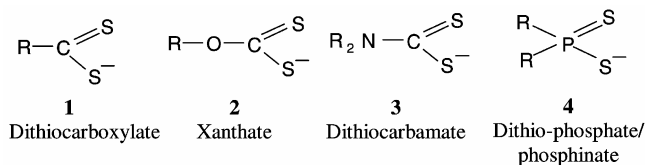e-mail: jainvk@barc.gov.in

Abstract. The chemistry of classical and organometallic complexes of gallium and indium with dithiolate ligands, i.e., dithiocarboxylates, xanthates, dithiocarbamates, dithiophosphates, dithiophophinates and dithioarsenates, has been reviewed. Synthesis, spectroscopic and structural aspects of these complexes are described. Their emerging role as single source molecular precursors for the preparation of metal sulfide thin films and nano-particles has been discussed.

Keywords. Gallium; indium; dithiocarboxylates; xanthates; dithiocarbamates; dithiophosphates; NMR; nanoparticles.

1. Introduction

1,1-Dithiolates (**1–4**) are one of the interesting families of ligands. They have been used extensively in classical and organometallic chemistry for several decades.[1-3] Although gallium(III) and indium(III) complexes with some of these ligands have been known since early 1940s,[4-7] their potential as single source molecular precursors for the preparation of metal sulfide thin films/nano-particles was exploited only in the last decade.[8,9] The III–VI materials exist in different stoichiometries and structures. Several of these materials are direct band semiconductors exhibiting a variety of interesting electronic and opto-electronic properties which have potential applications (particularly M_2E_3; M = Ga or In; E = S, Se) in switching devices, photovoltaic and as passivating agents for III–V devices. This review intends to cover various aspects of gallium and indium dithiolate complexes so as to provide further acceleration to the subject area.
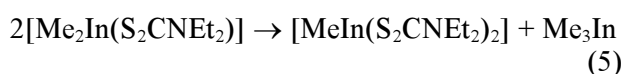

1	**2**	**3**	**4**
Dithiocarboxylate	Xanthate	Dithiocarbamate	Dithio-phosphate/ phosphinate

*For correspondence

2. Syntheses

Gallium(III) and indium(III) tris(dithiolates), $[M(S\frown S)_3]$ (M = Ga or In; $S\frown S = RCS_2^-$,[10-12] $ROCS_2^-$,[6,7,13] $R_2NCS_2^-$,[5,14-18] $(RO)_2PS_2^-$,[19-21] $R_2PS_2^-$[22-25] or $R_2AsS_2^-$[26-28]) are readily obtained by the reactions of metal halides with ammonium or alkali metal salts in non-aqueous or slightly acidic aqueous solutions. Metastable indium-113 diaklydithiocarbamates $[^{113m}In(S_2CNR_2)_3]$ (R = Et, Pr^n, Pr^i, Bu^n, Bu^i, 1/2(CH$_2$)$_5$ or 1/2CH$_2$CH$_2$O CH$_2$CH$_2$), required for *in vitro* studies, have been prepared by treatment of $^{113m}InCl_3$ with an aqueous solution of the ligand.[29] Otherless commonly employed methods involve (i) reductive cleavage of S–S bond of thiurams $[(R_2NCS_2)_2; R = Me, Et, Bz]$ with $GaH_3 \cdot NEt_3$,[30] (ii) oxidation of indium metal by tetra alkylthiuram disulfide (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i) either in refluxing xylene or in 4-methylpyridine at room temperature,[17,31] (iii) oxidation of InX (X = Cl, Br, I) by $(R_2NCS_2)_2$[17] and (iv) electrochemical oxidation[15] of appropriate metal anode (Ga or In) in acetonitrile or acetone solution of either $(R_2NCS_2)_2$ (R = Me or Et) or $(EtO)_2PS_2H$.

Several organometallic complexes with dithiolate ligands have also been prepared. They are synthesized by (i) alkane elimination reaction between R_3M and $S\frown SH$ (**1**) $(S\frown SH = R_2CS_2H$,[12,32] Me_2NCH_2 $CH_2CH_2(Me)NCS_2H$,[33] $(RO)_2PSSH$,[34] $R_2PSSH)$,[24,35,36] (ii) salt elimination reaction between R_2MX (X = Cl or OAc) and alkali metal salts[34,37-40] (**2**) and (iii) re-

distribution reactions (3, 4) of trialkylmetal with tris complexes.[39,41] The latter reaction is quite facile affording products in quantitative yields. This reaction has been extended to the preparation of chloro complexes, $[MCl_{3-n}\{S_2P(OR_2)\}_n]$ ($n = 1$ or 2). Depending on the stoichiometry of MCl_3 and $[M\{S_2P(OR)_2\}_3]$ both mono and dichloro derivatives are isolated as analytically pure products in quantitative yields.[20,21] The complex $[Me_2In(S_2CNEt_2)]$ disproportionates in methanol to give $[MeIn(S_2CNEt_2)_2]$ in 48% yield and Me_3In, although the formation of the latter has not been confirmed (5).[37] A similar disproportionation has been reported recently for gallium complexes $[Bu^t_2Ga(S_2CNR_2)]$.[38] Potentiometric titrations for determination of gallium and indium ions using dialkyldithiocarbamates have also been carried out.[42–46]

$$R_3M + S^\frown SH \rightarrow [R_2M(S^\frown S)] + RH \qquad (1)$$

$$[R_2MCl]_2 + 2S^\frown S^- \rightarrow 2[R_2M(S^\frown S)] + 2Cl^- \qquad (2)$$

$$2R_3M + M(S^\frown S)_3 \rightarrow 3[R_2M(S^\frown S)] \qquad (3)$$

$$R_3M + 2M(S^\frown S)_3 \rightarrow 3[RM(S^\frown S)_2] \qquad (4)$$

$$2[Me_2In(S_2CNEt_2)] \rightarrow [MeIn(S_2CNEt_2)_2] + Me_3In \qquad (5)$$

(R = Me, Et, Pr^i, Bu^t, etc.; M = Ga or In; $S^\frown S$ = dithiolate ligand)

3. Spectroscopy

Molecular weight determinations on $[In(S_2CAr)_3]$ in dmso[11] and $[R_2M(S_2PR_2)]$ (R = Ph or OR') in benzene[34,35] revealed their monomeric nature. Mass spectra of a number of dithiolate complexes have been reported and in general they are devoid of molecular ion peaks.[20,21,24,33,39,47,48] The mass spectra of tris complexes, $[M(S^\frown S)_3]$ ($M/S^\frown S$ = In/S_2CNMe_2; $In/S_2P(OR)_2$; $Ga/S_2P(OR)_2$)[20,21,48] exhibit peaks due to $[M(S^\frown S)_2]^+$, $[M(S^\frown S)_2S]^+$, $[M(S^\frown S)]^+$. The diorganometal dithiolate complexes, $[R_2M(S^\frown S)]$ (R = Me, Et, neopentyl, M = Ga or In, $S^\frown S$ = S_2CNR_2)[33,39] show a prominent peak due to $[RM(S^\frown S)]^+$, besides other fragment ions. Based on the mass spectral data of $[Bu^t_2Ga(S_2PPh_2)]$, a dimeric structure has been suggested, although the complex has not been isolated.[24] Unlike organometallic derivatives, the chloro complexes, $[MCl_{3-n}\{S_2P(OR)\}_n]$ ($n = 1$ or 2), display molecular ion peaks in their mass spectra.[20,21]

The M–S stretching in the IR spectra of a variety of complexes have been assigned in the regions of 310–352 (M = In)[49] and 365–380 cm^{-1} (M = Ga).[33] The Ga–C and In–C stretching vibrations appear in the regions 530–606[33,35] and 450–521 cm^{-1} [33,37] respectively.

Both classical and organometallic derivatives have been characterized by NMR spectroscopy. The ^1H and ^{13}C NMR spectra in general show expected resonances with normal splitting features.[12,17,20,21,41] The following trend in the NMR spectra of analogous complexes is quite evident:

(i) The $^{31}P\{^1H\}$ NMR signal is shifted downfield with increasing number of dithiophosphate ligand on a metal atom and appear in the following order:[12,20,21]

$$[X_2M\{S_2P(OR)_2\}] < [XM\{S_2P(OR)_2\}_2] <$$
$$[M\{S_2P(OR)_2\}_3]$$
(M = Ga or In; X = Cl, Me, Et)
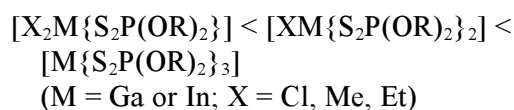
(ii) The CS_2 resonances in the $^{13}C\{^1H\}$ NMR spectra are downfield shifted in the following order of dithio ligand:[41]

$$R_2NCS_2 > ROCS_2 > RCS_2$$

(iii) The methyl-metal resonance in ^1H and ^{13}C NMR spectra is progressively downfield shifted on replacing a methyl group by a dithio ligand:[41]

$$[Me_3M.OEt_2] > [Me_2M(S^\frown S)] > [MeM(S^\frown S)_2]$$

Variable temperature ^1H NMR spectra of $[M(S_2CN Bz_2)_3]$, $[M(S_2CNMePh)_3]$[50] and $[In(S_2CNPr^i_2)_3]$[51,52] have been investigated. The Me–N signal in the spectra of $[M(S_2CNMePh)_3]$ (M = Ga or In) appears as a singlet down to −50°C, and around −85°C, peak broadens with an asymmetric shoulder due to slow *cis-trans* isomerization process.[50] However, in the case of benzyl derivatives, $[M(S_2CNBz_2)_3]$, only one CH_2 resonance is observed down to −100°C due to fast inversion process.[50] The ^1H NMR spectrum of $[In(S_2CNPr^i_2)_3]$ displays three broad resonances at δ 1·50 (Me) and 4·00, 5·10 (CH) ppm at room temperature.[17] However, below −50°C, spectrum exhibits two doublets of equal intensity for methyl and two septets for methine protons.[51] These doublets and septets coalesce to a single doublet and a septet in the temperature range −50 to 15°C.[51] These results have been interpreted in terms of inequivalance of isopropyl groups arising

from a gear like (180°) rotation around C–N single bond (scheme 1).[51]

The [71]Ga NMR (I = 3/2, natural abundance = 39·6%) spectra of [Ga(S$_2$CNR$_2$)$_3$] have been studied.[18] The [71]Ga NMR signal is considerably shielded relative of [Ga(H$_2$O)$_6$]$^{3+}$. The nature of the substituents on the nitrogen atom is reflected on the [71]Ga NMR chemical shifts and ½ line widths of the resonances (table 1).[18] The [71]Ga NMR resonances for the complexes are considerably broadened as compared to the reference material, [Ga(H$_2$O)$_6$]$^{3+}$. This broadening for complexes as compared to reference [Ga(H$_2$O)$_6$]$^{3+}$ which has a symmetrical electric field gradient around the quadrupolar [71]Ga nucleus, has been attributed to distortion in ideal octahedral geometry (see X-ray crystallography).

4. Structures

A large number of gallium and indium complexes with dithiolate ligands have been structurally characterized (table 2).[12,18,21–23,25,30,31,33,38,39,47,49,52–67] The complexes are discrete monomers and in general have distorted geometries owing to the restricted bite of the dithio ligands. The S–M–S angle of the chelating dithio ligands varies between 66·6 and 81·7°, the
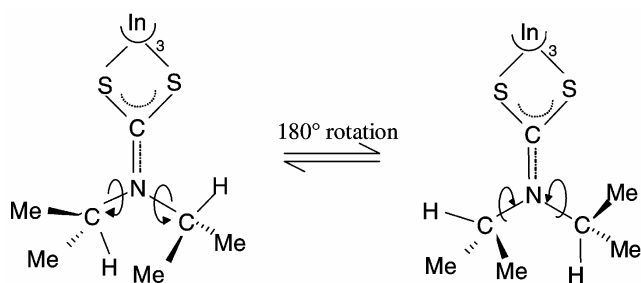
Scheme 1.

**Table 1.** [71]Ga NMR chemical shifts of gallium(III) dithiocarbamates and reference materials[18].

Complexes	δ^{71}Ga (ppm)	1/2 line width (Hz)
[Ga(H$_2$O)$_6$]$^{3+}$	0·0	28
Na[Ga(OH)$_4$]	223·3	123
[Ga(S$_2$CNMe$_2$)$_3$]	−94·6	1100
[Ga(S$_2$CNEt$_2$)$_3$]	−83·9	1730
[Ga(S$_2$CNPr$^i_2$)$_3$]	−64·5	2220
[Ga(S$_2$CN(CH$_2$CH$_2$)$_2$O)$_3$]	−76·2	2298
[Ga{S$_2$CN(CH$_2$CH$_2$)$_2$NMe}$_3$]	−80·7	2822
[GaCl{S$_2$CN(CH$_2$CH$_2$)$_2$O}$_2$]	77·2	3875

angle being larger for gallium complexes than the corresponding indium derivatives owing to the difference in ionic radii of two metals (ionic radii of M^{3+}: 0·62 (Ga), 0·81 (In) Å). The S–M–S angle also increases on replacing –CS$_2^-$ fragment by >PS$_2^-$ through >AsS$_2^-$. The tris complexes of gallium and indium are isostructural in nature and have a six coordinate metal atom with the exception of [Ga(S$_2$PBu$^i_2$)$_3$] which has a distorted tetrahedral geometry around gallium (figure 1).[25] The geometries of tris complexes can be trigonal prismatic or distorted octahedral (scheme 2). In dithiocarbamate complexes, the C–N distances are significantly shorter than the single N–C bond, due to delocalization of $p\pi$ electrons of C=S linkage in ${}_S^S{>}{=}N$ [53,54]. The In–S bond lengths in the chelates are usually similar, but the Ga–S distances show considerable difference. The tris(xanthate) complexes consist of enantiomeric pairs of discrete [M(S$_2$COR)$_3$] with the geometry of the metal atom between trigonal prismatic and octahedral.[55,56]

The complexes [R$_2$M(S⌢S)] adopt a distorted tetrahedral configuration defined by a chealting dithiolate ligand and two alkyl groups. The S–M–S angle is smaller than the C–M–C angle.[38,39] The complex, [Et$_2$In(S$_2$CN(Me)CH$_2$CH$_2$CH$_2$NMe$_2$)]$_n$, however, has a polymeric structure owing to the chelation of dithiocarbamate ligand and NMe$_2$ coordination. The indium atom adopts a distorted trigonal bipyramidal configuration (figure 2).[33] A similar configuration is observed for [Et$_2$In(SOCNEt$_2$)]$_n$. The two ethyl carbons and the sulfur atom lie at the equatorial plane and the ligand behaves in a chelating bridging (through O) fashion.[57]

The complexes [XM(S⌢S)$_2$] (M = Ga or In, X = Cl or alkly group) adopt a five coordinate configuration with the geometries which are quite often intermediate between trigonal bipyramid and square pyramid. The gallium and indium atom in [MCl(S$_2$CNR$_2$)$_2$] lie above (0·46 Å for Ga and 0·79 Å for In) the mean S$_4$ plane of a distorted square pyramidal configuration.[49] The crystals of [MeGa(S$_2$Ctol)$_2$] have two crystallographically independent molecules. The two asymmetrically chelated dithiocarboxylate ligands
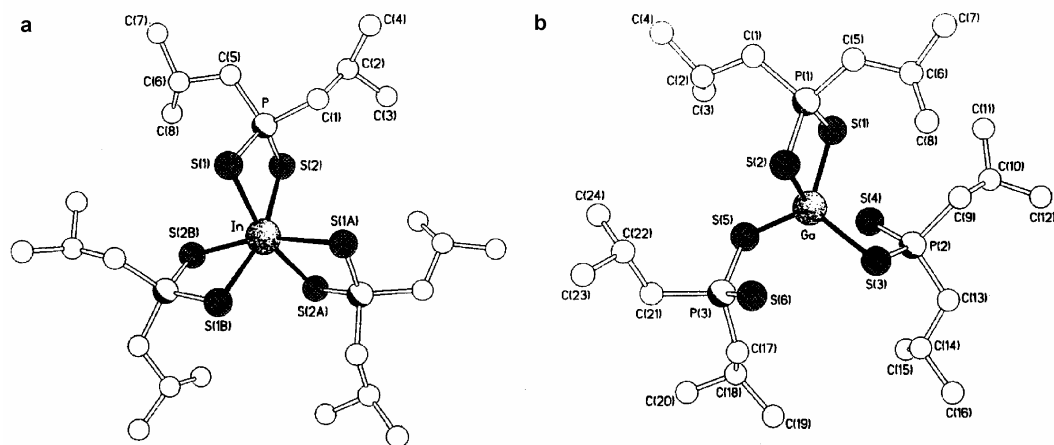

M = Ga, In; X = Cl, Me, Et; S⌢S = RCS$_2$, ROCS$_2$, R$_2$NCS$_2$, (RO)$_2$PS$_2$
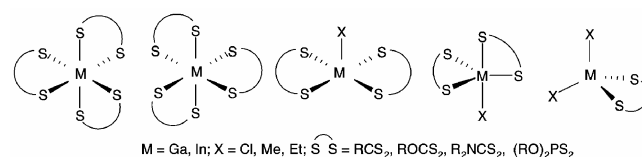
Scheme 2.

Figure 1. Structure of [M(S$_2$PBu$^i_2$)$_3$] (M = In (**a**); Ga (**b**)).[25]
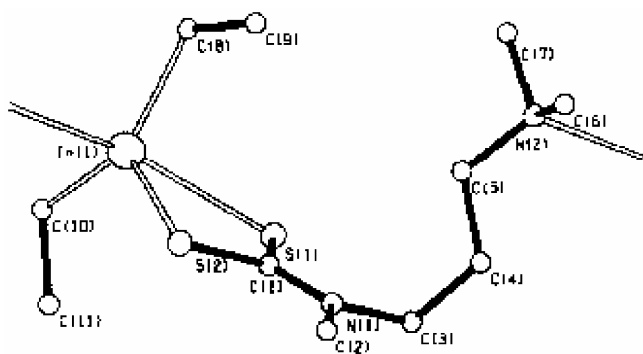
Figure 2. Molecular structure of [Et$_2$In(S$_2$CN(Me) CH$_2$CH$_2$CH$_2$NMe$_2$)]$_n$.[33]
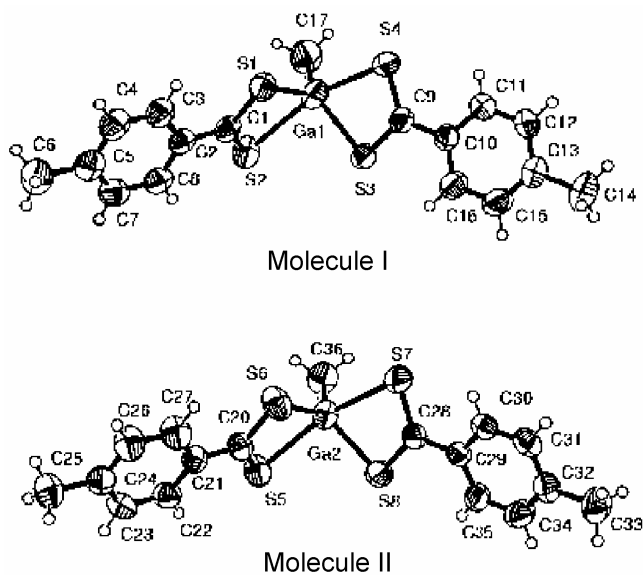

Figure 3. Structure of [MeGa(S$_2$Ctol)$_2$][12].

differ significantly in each molecule. The two shorter Ga–S distances are similar (av. 2·317 Å) in each molecule but the longer ones differ significantly (figure 3).[12]

The complexes [In{S$_2$P(OR)$_2$}{(SCH$_2$CH$_2$)$_2$O}]$_2$ (R = Et, Pr^i) have dimeric structures.[47,60] The indium atoms adopt a distorted octahedral configuration defined by a S$_5$O donor set with the non-planar central In$_2$S$_2$ core. Each oxydiethanethiolate ligand is tetradentate. The complexes [GaCl$_2$(S$_2$CNR$_2$)(4-Mepy)$_2$] (R = Me or Et)[58,59] adopt a distorted octahedral configuration in which roughly coplanar neutral 4-methyl pyridine (4-Mepy) ligands are mutually trans; while dithiocarbamate is asymmetrically chelated.

5. Thermal studies

Thermal behaviour of several dithiolate complexes has been studied by thermogravimetric technique.[17,62,68–71] Tris(xanthate) complexes of indium undergo a single step decomposition leading to the formation of In$_2$S$_3$.[71] Dithiocarbamate complexes undergo either a single step[17] or two closely spaced steps decomposition in the temperature range 239–389°C. Two pathways leading to the formation of either indium metal (R = Et, Pr^n, Bu^i) or In$_2$S$_3$ (R = Me, Pr^n, Bu^i) have been identified.[17] However, a later TG study showed that [In(S$_2$CNEt$_2$)$_3$] yields InS rather than the indium metal.[48] The complex [In(S$_2$CNBz$_2$)$_3$] on pyrolysis releases CS$_2$ and benzyl moieties in the gas phase leaving behind bulk In$_2$S$_3$.[62,69] Thermal decomposition of gallium dithiocarbamates is far less straightforward and often leaves a residue with much higher

Table 2. Gallium and indium dithiolate complexes characterized by single crystal X-ray diffraction analysis.

Compound	Geometry	Data	Ref.
[Ga(S$_2$COEt)$_3$]	Distorted octahedral	Ga–S = 2·405 (2), 2·465 (2) Å S–Ga–S = 73·50 (6)°	55
[Ga(S$_2$CNMe$_2$)$_3$]·CH$_2$Cl$_2$	Distorted octahedral	Ga–S = 2·418 (2) – 2·449 (2) Å S–Ga–S = 73·7° (av)	30
[Ga(S$_2$CNEt$_2$)$_3$]·2CHCl$_3$	Distorted octahedral	Ga–S = 2·421 (4) – 2·437 (4) Å S–Ga–S = 73·6° (av)	30
[Ga(S$_2$CNEt$_2$)$_3$]	Distorted octahedral	Ga–S = 2·408 (2) – 2·466 (1) Å S–Ga–S = ~73°	54
[Ga{S$_2$CN(CH$_2$CH$_2$)$_2$O}$_3$]	Distorted octahedral	Ga–S = 2·4223 (13) – 2·4544 (9) Å S–Ga–S = ~73·5°	18
[Ga(S$_2$CN(C$_4$H$_4$)}$_3$]	Distorted octahedral	Ga–S = 2·412 (2) – 2·471 (2) Å S–Ga–S = 73.6° (av)	49
[Ga(S$_2$CNBz$_2$)$_3$]	Octahedral	Ga–S = 2·389 (2) – 2·484 (3) Å S–Ga–S = 73·8° (av)	30
[Ga(S$_2$PBu$^i_2$)$_3$]	Distorted octahedral	Ga–S = 2·253 (3) – 2·337 (3) Å S–Ga–S = 87·03 (9)°	25
[In(S$_2$Ctol)$_3$]	Distorted octahedral	In–S = 2·5900 (14) – 2·6104 (16) Å S–In–S = 68·73 (4)°	64
[In(S$_2$COEt)$_3$]	Distorted octahedral	In–S = 2·574 (1), 2·622 (1) Å S–In–S = 69·77 (4)°	55
[In(S$_2$COPr^i)$_3$]	Distorted octahedral	In–S = 2·576 (2) – 2·625 (2) S–In–S = 69·7°	56
[In(S$_2$CNMe$_2$)$_3$]1/2pyMe-4	Distorted octahedral	P. hivin 1 a = 9·282(1), b = 10·081 (1), c = 12·502 Å; α = 73·91, (1)° β = 70·21 (1)° γ = 85·84 (1)°	31
[In(S$_2$CNEt$_2$)$_3$]	Trigonal prismatic	In–S = 2·582 (2) – 2·611(2) Å S–In–S = 69·5°	54
[In(S$_2$CNPr$^i_2$)$_3$]	Distorted octahedral	In–S = 2·583 (2) – 2·617 (2) Å S–In–S =68·5° (av)	52
[In{S$_2$CN(CH$_2$CH$_2$)$_2$NMe}$_3$]	Distorted octahedral	In–S = 2·582 (5), 2·575 (6) Å S–In–S = 70·21 (7)°	63
[In(S$_2$CN–C$_5$H$_{10}$)$_3$]	Trigonal prismatic	In–S = ~2·59 Å (all similar) S–In–S angle ~69°	53
[In(S$_2$CNBz$_2$)$_3$]	Octahedral	In–S = 2·5669 (6) – 2·6189 (6) Å S–In–S = 69·9° (av)	62
[In{S$_2$CN(C$_4$H$_4$)$_3$}]	Distorted octahedral	In–S = 2·597 (2) – 2·607 (2) Å S–In–S = 69·5° (av)	52
[In{S$_2$CN(CH$_2$CH$_2$)$_2$O}$_3$]	Distorted octahedral	In–S = 2·580 (2) – 2·615(2) Å S–In–S = ~69·5°	18
[In(S$_2$AsMe$_2$)$_3$]	Octahedral	In–S = 2·602 (5) – 2·675 (5) Å S–In–S = 80·6° (av)	67
[In(S$_2$AsPh$_2$)$_3$]	Octahedral	In–S = 2·608 (3) – 2·668 (3) Å S–In–S = 80·0 (1) – 81·7 (1)°	67
[In(SOCNEt$_2$)$_3$]	Distorted trigonal prismatic	In–S = 2·486 – 2·533 (2) Å	57
[In(S$_2$PMe$_2$)$_3$]	Distorted octahedral	In–S = 2·599 (2) – 2·643 (2) Å S–In–S = 77·14 (6) – 78·25 (6)°	23
[In(S$_2$P(OEt)$_2$]$_3$]	Distorted octahedral	In–S = 2·578(7) – 2·633(9) Å S–In–S = 77·1–79·1°	65

(*contd…*)

Table 2. (*Contd...*)

Compound	Geometry	Data	Ref.
$[In\{S_2P(OPr^i)_2\}_3]$	Distorted octahedral	In–S = 2·554 (4) – 2·652(5) Å S–In–S = 77·6 (1) – 79·4(2)°	21
$[In(S_2PBu^i_2)_3]$	Trigonally distorted octahedral	In–S = 2·6493 (9), 2·6100 (8) Å S–In–S = 77·53 (2)°	25
$[In(S_2PEt_2)_3]$	Trigonally distorted octahedral	In–S = 2·603 (1) – 2·638 (1) Å S–In–S = 77·28 – 77·72 (4)°	22
$[In(S_2PPh_2)_3]$	Distorted octahedral	In–S = 2·566 (6) – 2·622 (6) Å S–In–S = 77·7 – 78·4°	23
$[GaCl(S_2CNMe_2)_2]$	Distorted square pyramidal	Ga–Cl = 2·209 (1), Ga–S = 2·340(1) – 2·440 (1) Å	49
$[MeGa(S_2Ctol)_2]$	Intermediate between trigonal bypyramidal and square pyramidal	Ga–S = 2·3111 (18) – 2·6677 (19) Å S–Ga–S = 71–73°	12
$[InCl(S_2CNPr^i_2)_2]$	Square pyramidal	In–Cl = 2·380 (2), In–S = 2·533(1)–2·561(1) Å	49
$[GaCl_2(S_2CNEt_2)(4\text{-Mepy})_2]$	Octahedral	Ga–S = 2·479 Å S–Ga–S = 72·0°	58
$[GaCl_2(S_2CNMe_2)(4\text{-Mepy})_2]$	Distorted octahedral	Ga–S = 2·470 Å; Ga–Cl = 2·281 Å Ga–N = 2·149 Å S–Ga–S = 74·40 (7)°	59
$[Bu^tGa(S_2CNPr_2)_2]$	Distorted trigonal bypyramidal	Monoclinic, $P2_1/c$ a = 9·786 (1), b = 29·218 (3), c = 9·452 (1) Å; β = 108·379 (9)°	61
$[Bu^t_2Ga(S_2CNMe_2)]$	Distorted tetrahedral	Ga–S = 2·379 (5), 2·425 (5) Å S–Ga–S = 74·9 (2)°	38
$[Bu^t_2Ga(S_2CNEt_2)]$	Distorted tetrahedral	Ga–S = 2·389 (4), 2·379 (4) Å S–Ga–S = 75·6	38
$[(Pr^iO)Ga(S_2CNPr_2)_2]$	Distorted trigonal bypyramidal	Monoclinic, $P2_1/c$ a = 10·980 (3), b = 15·673 (4), c = 12·461 (1) Å, β = 97·47 (2)°	61
$[Et_2In(SOCNEt_2)]_n$	Distorted trigonal bypyramidal	In–S = 2·567 (1) Å	57
$[Me_2In(S_2CNEt_2)]$	Distorted tetrahedral	In–C = 2·14 (av) Å In–S = 2·56 (10), 2·68 (10) Å S–In–S = 68·8 (3)°	39
$[Et_2In(S_2CNEt_2)]$	Distorted tetrahedral	In–C = 2·15 (2), 2·22 (2) Å In–S = 2·57 (4), 2·60 (3) Å S–In–S = 68·5 (10)°	39
$[Et_2In(S_2CN(Me)CH_2CH_2CH_2NMe_2)]$	Distorted trigonal bipyramidal	In–S = 2·59 (1), 2·79 (1) Å S–In–S = 66·56 (4)°	33
$[In(S_2CNEt_2)_2\{(SePPr^i_2)_2N\}]$	Distorted octahedral	In–S = 2·592 (7)–2·648 (6) Å S–In–S = 68·6 (av)°	66
$[In(S_2PBu^i_2)_2\{(SePPr^i_2)_2N\}]$	Distorted octahedral	In–S = 2·649 (2)–2·665 (2) Å S–In–S = 76·0 (av)°	66
$[In\{S_2P(OPr^i)_2\}(SCH_2CH_2)_2O]_2$	Distorted octahedral	Monoclinic, $P2_1/c$ a = 8·962 (5), b = 15·222 (8), c = 27·54 (1) Å, β = 93·59 (6)°	60
$[In\{S_2P(OEt)_2\}(SCH_2CH_2)_2O]_2$	Distorted Octahedral	In–S = 2·416 (2) – 2·754 (1) Å S–In–S = 76·49 (5)°	47
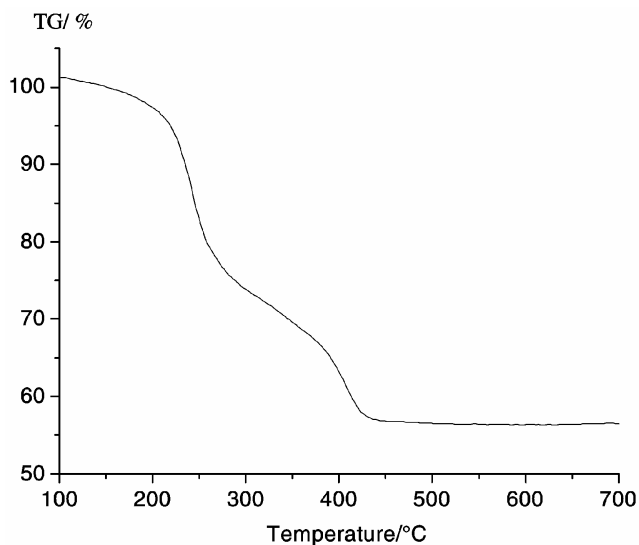
Figure 4. TG curve of [Me$_2$In(S$_2$Ctol)].[12]

weight than expected for Ga$_2$S$_3$.[70] Diorganoindium dithiocarboxylates undergo a two step decomposition with the formation of β-In$_2$S$_3$ as revealed by TG analysis (figure 4).[12]

6. Applications as molecular precursors for metal sulfides

Highly oriented films of α-In$_2$S$_3$ have been deposited on glass, GaAs (100), InP (111) substrate using asymmetric dithiocarbamates, [In(S$_2$CNMeR)$_3$] (R = Bu^n, Hex^n) in the temperature range of 450–500°C by low pressure MOCVD method.[72] The complexes [In(S$_2$CNEtBu)$_3$] and [In{S$_2$C(2-Et-piperdine)}$_3$] have been used as single source MOCVD precursors for deposition of β-In$_2$S$_3$ films on a glass substrate. Depending on the film thickness and grain size, the optical band gap varies between 2·0 and 2·4 eV.[73] Spray CVD on a copper substrate using [In(S$_2$CNBz$_2$)$_3$] produces CuInS$_2$ films.[62]

The complex [Bu$^t_2$Ga(S$_2$CNMe$_2$)] has been used for deposition of distorted hexagonal wurtzite phase of GaS by atmospheric pressure MOCVD (APMOCVD).[38] Under similar conditions [Bu$^t_2$Ga(S$_2$CNEt$_2$)] and [Bu$^t_2$Ga(S$_2$CNMe$_2$)] at low pressure, however, afford gallium rich sulfide films. Similar behaviour has been observed for other dithiocarbamate complexes of gallium.[38] The precursor, [Me$_2$Ga(S$_2$CNEt$_2$)] at 400°C yields golden colour gallium sulfide films which could not be characterized fully.[36] Low pressure MOCVD has been employed to deposit α-Ga$_2$S$_3$

films on GaAs(111) substrate at 500°C using [Ga{S$_2$CNMe(c-Hx)}$_3$] as a precursor.[74]

Diorgano indium dithiocarbamates[39,41,75] and xanthates[41] have been successfully used as precursors for the preparation of indium sulfide films and nanoparticles. The nature of the precursors has a pronounced effect on the composition and phase of resulting sulfide. The complexes [R$_2$In(S$_2$CNEt$_2$)] (R = Me, Et, neopentyl) have been used for the preparation of indium sulfide films on gallium arsenide (100) substrate in the temperature range of 325–425°C.[39] The methyl complex at 325°C gives cubic β-In$_2$S$_3$ films but at higher temperatures monoclinic In$_6$S$_7$ and InS phases are formed.[39] Decomposition of [Me$_2$In(S$_2$CNPr$^i_2$)] at 450°C yields amorphous InS.[41] In$_2$S$_3$ nano-rods have been deposited on a glass substrate at 450°C by aerosol assisted CVD using [Et$_2$In(S$_2$CNMeBu^n)].[75] Effects of annealing and decomposition temperature of indium sulfide films prepared from [In(S$_2$CNEt$_2$)$_3$] have been studied by synchrotron radiation diffraction.[76] Both [Me$_2$In (S$_2$COPr^i)] and [MeIn(S$_2$COPr^i)$_2$] at 450°C under flowing nitrogen in a furnace give a mixture of tetragonal and cubic β-In$_2$S$_3$.[41]

The complexes [In(S$_2$COR)$_3$] have been employed for the preparation of β-In$_2$S$_3$ films on a glass substrate[77] and nanoparticles.[71] Pyrolysis of [In(S$_2$COR)$_3$] (R = Me, Et, Pr^n, Bu^s) in refluxing ethylene glycol affords yellow, orange cubic β-In$_2$S$_3$ nanoparticles which have been characterized by XRD, XPS and TEM measurements. The highly blue shifted emission (440 nm) in the PL spectra of these particles relative to the bulk material (620 nm) has been attributed to quantum confinement of the nanoparticles.[71]

7. Summary and conclusion

Tris dithiolate complexes of gallium and indium are usually prepared by the reactions of metal halides with ammonium/alkali metal salts of a dithio acid, whereas organometallic derivatives are obtained conveniently by a redistribution reaction between R$_3$M and [M(S⌒S)$_3$]. These complexes are readily characterized by NMR spectroscopy and the spectra, in general, exhibit expected resonances and peak multiplicities. Both classical and organometallic dithiolates are discrete monomeric complexes adopting distorted geometries owing to small bite of the ligand. The xanthate and dithiocarbamate complexes of indium have been used successfully as molecular precursors for

the preparation of In_2S_3 thin films and nano-particles. Different phases of In_2S_3 can be generated either by changing the precursors or by subtle variation in pyrolytic conditions. Although gallium complexes have also been used as precursors, their full potential for the preparation of compositionally and phase pure gallium sulfides are yet to be realized.

Acknowledgements

References

1. Wasson J R, Woltermann G M and Stoklosa H J 1973 *Top. Curr. Chem.* **35** 65
2. Livingstone S E 1987 in *Comprehensive coordination chemistry* (eds) G Wilkinson, R D Gillard, J A McCleverty (Oxford: Pergamon Press) vol 2, pp 633–659
3. Haiduc I 2004 In *Comprehensive coordination chemistry – II* (eds) J A McCleverty and T J Meyer (Elsevier) vol 1, Chapter 1.15, pp 349–376
4. Ensslin F and Dreyer H 1942 *Z. Anorg. Allg. Chem.* **249** 119
5. Delepine M 1951 *Ann. Chim. Appl.* **6** 633; Delepine M 1952 *Chem. Abst.* **46** 3442i
6. Delepine M 1951 *Ann. Chim. Appl.* **6** 645; Delepine M 1952 *Chem. Abst.* **46** 3443a
7. Sutton G J 1950 *Roy. Aust. Chem. Inst. J. Proc.* **17** 249; Sutton G J 1951 *Chem. Abstr.* **45** 2873e
8. Barron A R 1995 *Adv. Mat. Optics Elect.* **5** 245
9. Lazell M, O'Brien P, Otway D J and Park J H 2000 *J. Chem. Soc., Dalton Trans.* 4479
10. Furlani C and Luciani M L 1968 *Inorg. Chem.* **7** 1586
11. Singh S K, Singh Y, Rai A K and Mehrotra R C 1989 *Polyhedron* **8** 633
12. Ghoshal S, Jain V K, Dutta D P, Phadnis P P and Nethaji M 2006 *J. Organomet. Chem.* **691** 5838
13. Galsbol F and Schaffer C E 1967 *Inorg. Synth.* **10** 44
14. Srivastava T N, Kumar V and Srivastava O P 1978 *Natl. Acad. Sci. Lett.* **1** 97; Yang T, Tao W, Yang Y and Han Y 1992 *Huaxue Shiji* **14** 334; Yang T, Tao W, Yang Y and Han Y 1993 *Chem. Abst.* **118** 204062m
15. Geloso C, Kumar R, Lopez-Grado J R and Tuck D G 1987 *Can. J. Chem.* **65** 928
16. Abram S and Abram U 1988 *Inorg. Chim. Acta* **153** 135
17. Oliveira M M, Pessoa G M, Carvalho L C, Peppe C, Souza A G and Airoldi C 1999 *Thermochimica Acta* **328** 223
18. Dutta D P, Jain V K, Knoedler A and Kaim W 2002 *Polyhedron* **21** 239
19. Ahmad A, Srivastava G and Mehrotra R C 1985 *Inorg. Chim. Acta* **97** 159
20. Pahari D and Jain V K 1997 *Main Group Met. Chem.* **20** 691
21. Pahari D, Jain V K and Patel R P 1998 *Main Group Met. Chem.* **21** 261
22. Svensson G and Albertsson J 1989 *Acta Chem. Scand.* **43** 511
23. Zukerman-Schpector J, Haiduc I, Silvestru C and Cea-Olivares R 1995 *Polyhedron* **14** 3087
24. Landry C C, Hynes A, Barron A R, Haiduc I and Silvestru C 1996 *Polyhedron* **15** 391
25. Park J H, O'Brien P, White A J P and Williams D J 2001 *Inorg. Chem.* **40** 3629
26. Forster M, Hertel and Kuchen W 1970 *Angew Chem.* **9** 811
27. Casey A T, Ham N S, Mackey D J and Martin R L 1970 *Aust. J. Chem.* **23** 1117
28. Muller A and Werle P 1971 *Chem. Ber.* **104** 3782
29. Abram S, Abram U, Spies H and Munze R 1985 *Int. J. Appl. Radiat. Isotopes* **36** 653
30. Andrews P C, Lawrence S M, Raston C L, Skelton B W, Tolhurst V A and White A H 2000 *Inorg. Chim. Acta* **300–302** 56
31. Clark E B, Breen M L, Fanwick P E, Hepp A F and Duraj S A 2000 *J. Coord. Chem.* **52** 111
32. Weildlein J 1971 *Z. Anorg. Allg. Chem.* **386** 129
33. Haggata S W, Malik M A, Motevalli M and O'Brien P 1996 *J. Organomet. Chem.* **511** 199
34. Wieber M and Clarius T 1995 *Phosh. Sulfur Silicon* **102** 261
35. Coates G E and Mukherjee R N 1964 *J. Chem. Soc.* 1295
36. Schaible B, Haubold W and Weidlein J 1974 *Z. Anorg. Allg. Chem.* **403** 289
37. Maeda T and Okawara R 1972 *J. Organomet. Chem.* **39** 87
38. Keys A, Bott S G and Barron A R 1999 *Chem. Mater.* **11** 3578
39. Haggata S W, Malik M A, Motevalli M, O'Brien P and Knowles J C 1995 *Chem. Mater.* **7** 716
40. Prasad N, Dutta D P and Jain V K 2002 *Main Group Met. Chem.* **25** 677
41. Ghoshal S, Kushwah N P, Dutta D P and Jain V K 2005 *Appl. Organomet. Chem.* **19** 1257
42. Ivanova Z I, Sazhneva T V, Chebotarev V K and Shelepin O E 1974 *Zh. Anal. Khim.* **29** 466; Ivanova Z I, Sazhneva T V, Chebotarev V K and Shelepin O E 1974 *Chem. Abst.* **81** 32942x
43. Wyttenbach A and Bajo S 1979 *J. Inorg. Nucl. Chem.* **41** 867
44. Likussar W 1979 *Mikrochimica Acta* **2** 43; Likussar W 1979 *Chem. Abst.* **91** 167908t
45. Gevorgyan A M, Khadeev V A, Kostylev V S, Novgorodova and Yu N 1981 *Dokl. Akad. Nauk. USSR* 42; Gevorgyan A M, Khadeev V A, Kostylev V S, Novgorodova and Yu N 1981 *Chem. Abst.* **96** 192545h
46. Gencova O and Dimeski M 1989 *Glas. Hem. Tehnol. Maked.* **7** 67; Gencova O and Dimeski M 1991 *Chem. Abst.* **115** 149304c

47. Pahari D, Jain V K and Tiekink E R T 1998 *Main Group Met. Chem.* **21** 293
48. Hauser P J and Schreiner A F 1974 *Inorg. Chim. Acta* **6** 113
49. Bhattacharya S, Seth N, Srivastava D K, Gupta V D, Noth H and Thomann-Albach M 1996 *J. Chem. Soc., Dalton Trans.* 2815
50. Que Jr L and Pignolet L H 1974 *Inorg. Chem.* **13** 351
51. Lindmark A F and Fay R C 1983 *Inorg. Chem.* **22** 2000
52. Bhattacharya S, Seth N, Gupta V D, Noth H and Thomann M 1994 *Z. Naturforsch,* **B49** 193
53. Hauser P J, Bordner J and Schreiner A F 1973 *Inorg. Chem.* **12** 1347
54. Dymock K, Palenik G J, Slezak J, Raston C L and White A H 1976 *J. Chem. Soc., Dalton Trans.* 28
55. Hoskins B F, Tiekink E R T, Vecchiet R and Winter G 1984 *Inorg. Chim. Acta* **90** 197
56. Ghoshal S, Kumbhare L B, Wadawale A P and Jain V K and Nethaji M unpublished results
57. Horley G A, Chunggaze M, O'Brien P, White A J P and Williams D J 1998 *J. Chem. Soc., Dalton Trans.* 4205
58. Gordon E M, Hepp A F, Duraj S A, Habash T S, Fanwick P E, Schupp J D, Eckles W E and Long S 1997 *Inorg. Chim. Acta* **257** 247
59. Zhou X, Breen M L, Duraj S A and Hepp A F 1999 *Main Group Metal Chem.* **22** 35
60. Pahari D, Jain V K and Tiekink E R T 2000 *Z. Kristallogr. NCS* **215** 447
61. Keys A, Bott S G and Barron A R 1998 *J. Chem. Crystallogr.* **28** 629
62. Hehemann D G, Lau J E, Harris J D, Hoops M D, Duffy N V, Fanwick P E, Khan O, Jin M H C and Hepp A F 2005 *Mater. Sci. Eng.* **B116** 381
63. Dutta D P, Jain V K, Chaudhury S and Tiekink E R T 2001 *Main Group Met. Chem.* **24** 405
64. Ghoshal S, Wadawale A P, Jain V K and Nethaji M *Anal. Sci.* (in press)
65. Coggon P, Lebedda J D, McPhail A T, Palmer R A 1970 *Chem. Commun.* 78; Liu X Z, Xue H, Zhao J, Song Y L and Zang S L 1999 *Gaod. Xue. Haux. Xue*; **20** 196; Liu X Z, Xue H, Zhao J, Song Y L and Zang S L 1999 *Chem. Abst.* **130** 231382v
66. Malik M A, Afzaal M, O'Brien P and Halliwell M 2006 *Polyhedron* **25** 864
67. Silaghi-Dumitrescu L, Silaghi-Dumitrescu I, Haiduc I, Toscano R A, Gracia-Montalvo V and Cea-Olivares R 1999 *Z. Anorg. Allg. Chem.* **625** 347
68. Chernova A S, Yu Rakhlin M and Skopenko V V 1986 *Dok. Akad. Nauk Ukra RSR, Seriya* B53; Chernova A S, Yu Rakhlin M and Skopenko V V 1987 *Chem Abst.* **107** 16767u
69. Hoops M D, Hepp A F and Duffy N V 2003 *J. Undergraduate Chem. Res.* **2** 95
70. Brothers S M, Baird M J, Hepp A F and Duffy N V 2007 *J. Undergraduagte Chem. Res.* **6** 35
71. Dutta D P, Sharma G, Ghoshal S, Kushwah N and Jain V K 2006 *J. Nanosci. Nanotech.* **6** 235
72. O'Brien P, Otway D J and Walsh J R 1998 *Thin Solid Films* **315** 57
73. Lee S S, Yoon S H, Seo K W and Shim I W 2005 *Bull. Korean Chem. Soc.* **26** 1453; Lee S S, Yoon S H, Seo K W and Shim I W 2005 *Chem. Abst.* **144** 303865
74. Lazell M R, O'Brien P, Otway D J and Park J H 1999 *Chem. Mater.* **11** 3430
75. Afzaal M, Malik M A and O'Brien P 2004 *Chem. Commun.* 334
76. Bessergenev V G, Bessergenev A V, Ivanova E N and Kovalevskaya Y A 1998 *J. Solid State Chem.* **137** 6
77. Bessergenev V G, Ivanova E N, Kovalevskaya Y A, Gromilov S A, Kirichenko V N and Larionov S V 1996 *Inorg. Mater.* **32** 592