

Organo-gallium and indium complexes with dithiolate and oxo ligands: Synthesis, structures and applications

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Abstract. The chemistry of organo-gallium and indium complexes with dithiolate and internally functionalised oxo ligands has been explored. With 1,1-dithiolate ligands both classical and organometallic complexes of gallium and indium, $[M(S^{\cap}S)_3]$, $[RM(S^{\cap}S)_2]$ and $[R_2M(S^{\cap}S)]$ (where R = Me or Et; M = Ga or In; $S^{\cap}S = RCS_2, ROCS_2, R_2NCS_2$ and $(RO)_2PS_2$) have been isolated. Reactions of internally functionalised oxo ligands with $R_3M \cdot OEt_2$ afforded diorganometal complexes $[R_2ML]_n$. Molecular structures of several of these complexes have been established by single crystal X-ray diffraction analyses. Complexes derived from oxo ligands showed photoluminescence. They have been used as alkylating agents for C–C coupling reactions of aryl bromides in the presence of $PdCl_2(PPh_3)_2$. Indium dithiolate complexes have been used as molecular precursors for the preparation of mono dispersed β - In_2S_3 nanoparticles.

Keywords. Organo-gallium; organoindium; structures; In_2S_3 nanoparticles; photoluminescence; C–C coupling reactions.

1. Introduction

The chemistry of organo-gallium and indium compounds with group 16 ligands has been an active area of research for the last several years.^{1–3} The interest in these compounds stems from their rich structural diversity and their potential applications in catalysis⁴ and as molecular precursors for III–VI materials which have useful electronic and optical properties.^{5–7}

The following aspects of gallium and indium compounds have attracted our attention while executing a project on high purity materials of group III and V elements required for advanced technologies.

(i) Molecular precursor for β - In_2S_3 : Group III elements form numerous metal chalcogenides differing in composition and phases and find applications in opto-electronic and photovoltaic devices and catalysis. Among III–VI materials, β - In_2S_3 is a front-runner due to its desirable optical and acoustic properties and as a material of choice for passivating III–V films (e.g., GaAs). In view to develop low temperature synthesis of β - In_2S_3 mono-dispersed nano-crystals, molecular precursor route, a versatile strategy in materials synthesis, has been explored.

(ii) C–C coupling reactions: Carbon–carbon bond formation catalysed by palladium complexes is one

of the most important reactions in organic synthesis. In C–C coupling reactions of arylhalides, a variety of reagents are employed. Recently organoindium compounds have shown promising potential in C–C coupling reactions.⁴

(iii) Photoluminescence properties of organo-gallium and indium compounds: Since the discovery of *tris*(8-hydroxyquinolinolato)aluminium(III) (AlQ) as organic electro-luminescent material, there has been growing interest to design and develop metal chelates of high luminous efficiency capable of emitting different colours for OLED (organic light emitting diode) applications.⁸ Organometallic complexes derived from chelating ligands, such as substituted 8-hydroxyquinoline and azomethine linkages, are emerging as potential molecules for OLEDs.

In the above prospective we have explored the chemistry of gallium and indium compounds with 1,1-dithiolate and oxo ligands in the last few years. Salient features of this investigation are described here.

2. Results and discussion

2.1 1,1-Dithiolato-complexes

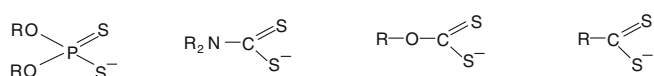
Both classical and organometallic complexes of gallium and indium with 1,1-dithiolate ligands (dithiophosphate, dithiocarbamate, xanthate, dithiocarboxy-

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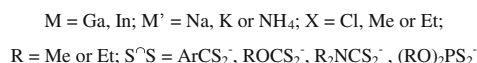
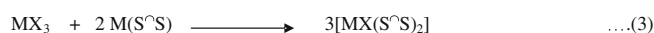
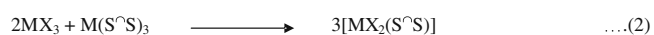
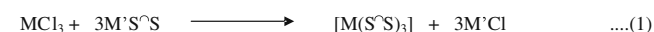
late) (scheme 1) have been synthesised employing reaction routes shown in scheme 2.⁹⁻¹⁷ Redistribution reaction has been quite facile for the synthesis of organometallic derivatives, affording mono- and di-organometal derivatives in quantitative yields.

These complexes have been characterised by NMR (¹H, ¹³C, ³¹P, and ⁷⁷Ga) and mass spectrometry and in some cases by single crystal X-ray crystallography. The ¹H and ¹³C NMR chemical shifts were sensitive to the nature and the number of dithiolato ligands on the metal atom. The Me-M resonance in the ¹H and ¹³C NMR spectra is progressively shifted downfield in the following order of substitution: Me₃M·OEt₂ > [Me₂M(S[⊖]S)] > [MeM(S[⊖]S)₂]. The mass spectra of these complexes did not show molecular ion peaks nor any peak higher than the molecular ions.^{10,11,15,18} The *tris* complexes exhibited peaks attributable to '[M(S[⊖]S)₂]⁺' species, while the organoindium complexes showed peaks due to 'M-Me' fragments.

Structures, established by X-ray crystallography, consist of discrete monomeric molecules and adopt distorted geometries (scheme 3) due to restricted bite of dithio ligand. The *tris* complexes of gallium and indium are isostructural in nature acquiring a distorted octahedral configuration (figure 1). The In-S distances in *tris* complexes of indium varies between 2.554(4) and 2.652(5) Å with the progressively opening up, though slightly, of S-In-S angle in the following series: [In(S₂Ctol)₃] (68.73(4)°); [In{S₂C(OPrⁱ)₃] (av 69.75°); [In(S₂CN(CH₂)₄NMe)₃] (70.21(7)°) and [In{S₂P(OPrⁱ)₂}₃] (av 77.9°).^{11,12,18,19} The complex [MeGa(S₂Ctol)₂] has two crystallographically independent molecules in the crystals, each have a five coordinated gallium atom. The geometry around gallium is



Scheme 1.



Scheme 2.

intermediate between trigonal bipyramidal and square pyramidal configurations.¹⁷

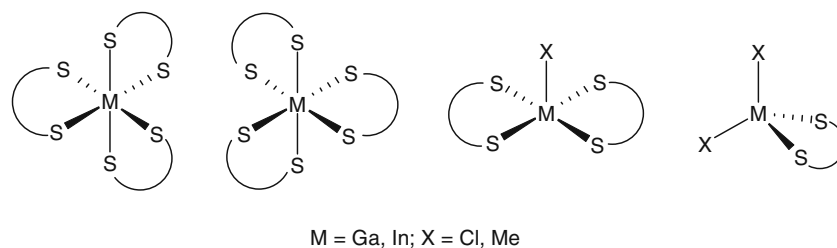
2.2 Thermal behaviour

Thermal behaviour of indium complexes has been investigated by thermogravimetric analysis.^{12,16-18} Indium *tris* xanthates and *tris* dithiocarboxylates undergo a single-step decomposition with the formation of In₂S₃ assessed by weight loss, EDAX and XRD pattern. Xanthates decomposed at much lower temperatures (~125°C) as compared to dithiocarboxylates (~190°C).^{16,18} Indium dithiocarbamates and [Me₂In(S₂Ctol)], however showed a two-step decomposition^{12,17} leading to the formation of In₂S₃.

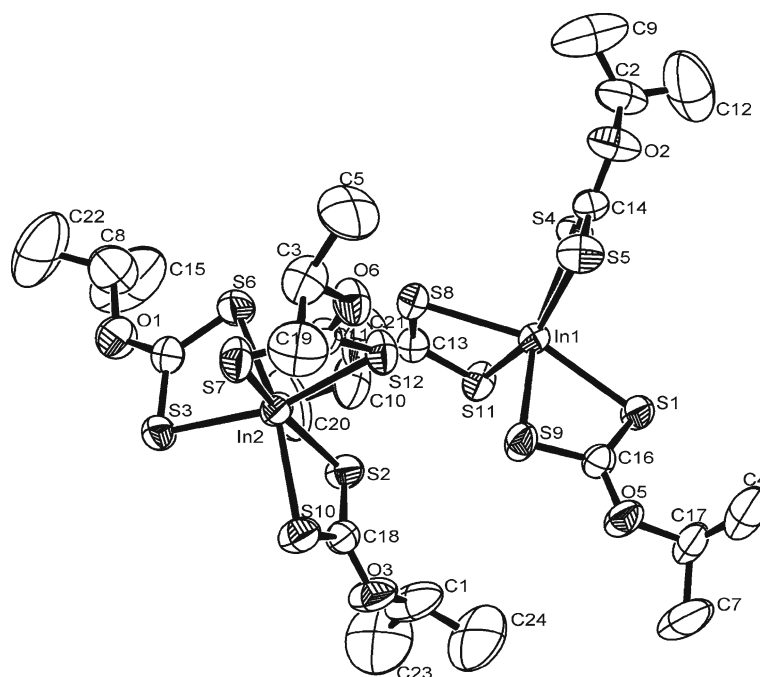
Pyrolysis of dithiocarboxylate, xanthate and dithiocarbamate complexes has been carried out in a furnace and in boiling organic solvents (ethylene glycol, hexadecylamine).¹⁶⁻¹⁸ Thermolysis of [In(S₂CPh)₃] in HDA at 300°C yields β-In₂S₃ with predominance of tetragonal phase (figure 2). Similarly a mixture of tetragonal and cubic β-In₂S₃ is obtained when [MeIn(S₂COPrⁱ)₂] or [Me₂In(S₂COPrⁱ)] are heated at 450°C in a furnace under a flowing nitrogen. However, thermolysis of indium *tris* xanthates in refluxing ethylene glycol proceeds smoothly to afford yellow orange nano-crystals of In₂S₃ which have spherical shape with the diameter varying in the range 19–30 nm (TEM studies).

2.3 Diorgano-gallium and indium complexes with oxo ligands

The reactions of triorganometal etherate with an appropriate internally functionalised anionic oxo ligand, viz. 2-(hydroxyalkyl)pyridines, N-heterocyclic carboxylic acids, 2-(2-hydroxyphenyl)oxazoline and 1-(2-hydroxyethyl)pyrazoles (scheme 4), in 1:1 molar ratio in benzene afforded readily dimeric diorganometal complexes containing central rectangular 'M₂(μ-O)₂' core (scheme 5).²⁰⁻²⁴ The mass spectra showed peaks higher than the formula weight suggesting their associated nature. Gallium and indium species can be identified readily from the characteristic isotopic pairs (⁶⁹Ga/⁷¹Ga; ¹¹³In/¹¹⁵In). The spectra in general exhibit peaks due to M-Me, M/2, R₂M⁺.²¹⁻²³ The diorgano-gallium complexes derived from 2-(2-hydroxyphenyl)oxazoline did not show any peak higher than the formula weight suggesting their monomeric nature.²²

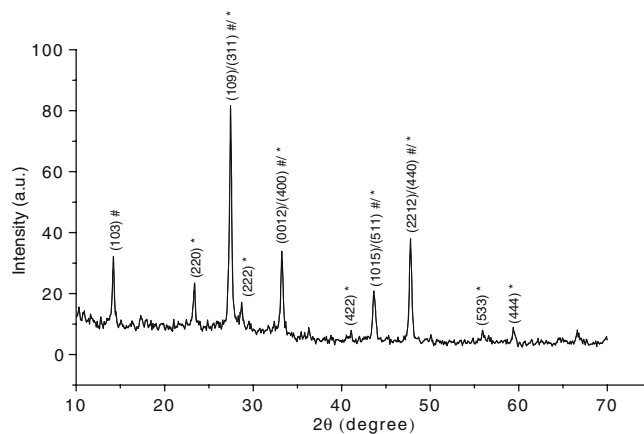


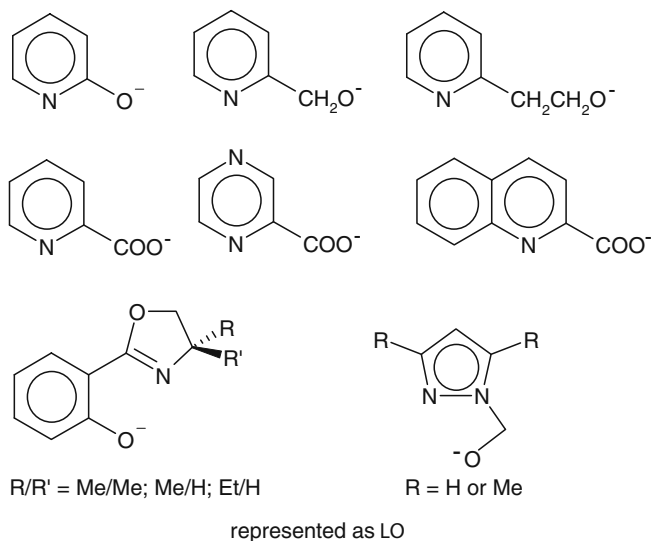
Scheme 3.

Figure 1. Crystal structure of $[\text{In}(\text{S}_2\text{COPr}^i)_3]$.

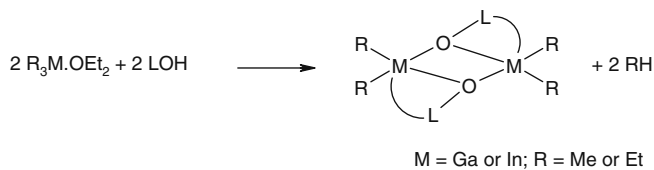
These complexes have been characterised by IR and NMR (^1H , ^{13}C) spectroscopy. The NMR spectra displayed expected resonances and peak multiplicities. The methyl-metal signals in the ^1H and ^{13}C NMR spectra appeared in the regions -0.40 to $+0.20$ ppm and -3.7 to -8.3 ppm, respectively with dimethylgallium signal being more shielded.

Molecular structures of a few complexes have been established by X-ray crystallography.^{22–24} The structures are comprised of an oxygen-bridged dimeric unit containing five coordinate metal atoms in a highly distorted geometry defined by C_2NO_2 donor atoms. The μ -oxo atoms derived from two different ligands form a central rectangular M_2O_2 core.^{22–24} The gallium complex, $[(\text{Me}_2\text{GaO}-\text{CH}_2-\text{dmpz})_2]$ (figure 3) when recrystallised in open from dichloromethane, atmospheric

Figure 2. XRD pattern of $\beta\text{-In}_2\text{S}_3$ (# Tetragonal, * Cubic) obtained from solvolysis of $[\text{In}\{\text{S}_2\text{CPh}\}_3]$ in HDA.



Scheme 4.



Scheme 5.

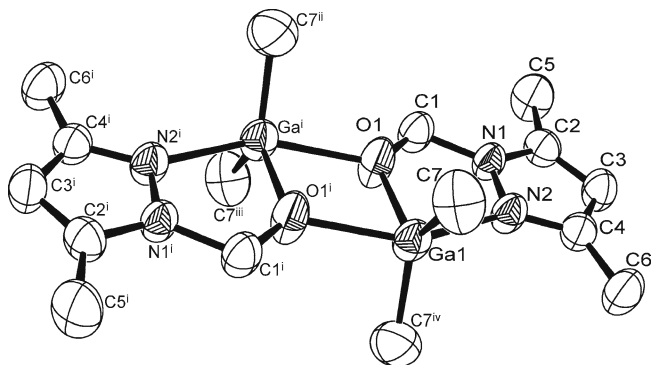
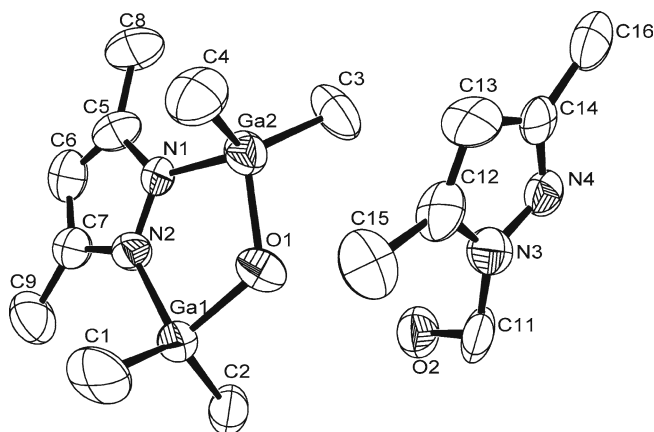
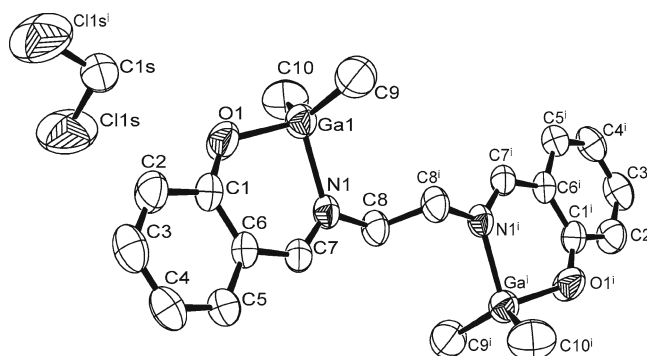
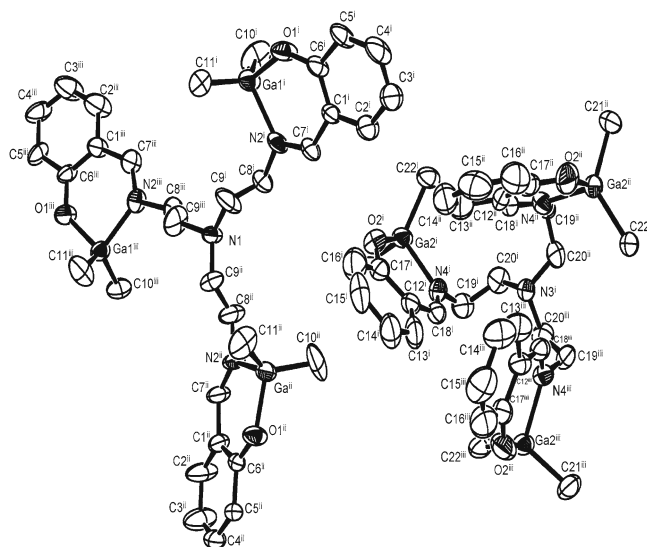
Figure 3. Crystal structure of $[Me_2GaO-CH_2dmpz]_2$.Figure 4. X-ray structure of $[\{Me_2Ga\}_2(\mu-OH)(\mu-dmpz)] \cdot HOCH_2dmpz$.Figure 5. Crystal structure of $[(Me_2Ga)_2(O-(C_6H_4)CH=N-CH_2-)] \cdot CH_2Cl_2$ grown from dichloromethane.Figure 6. Crystal structure of $[(Me_2GaO-(C_6H_4)CH=N-CH_2-CH_2-)_3N]$ grown from dichloromethane.

Table 1. Excitation and emission maxima of diorgano-gallium and indium complexes.

Compounds	Excitation λ in nm	Emission λ in nm
[Me ₂ Ga(O ₂ C–C ₅ H ₄ N)] ₂	257	368
[Et ₂ Ga(O ₂ C–C ₅ H ₄ N)] ₂	252	369
[Me ₂ In(O ₂ C–C ₅ H ₄ N)] ₂	257	371
[Me ₂ Ga(O ₂ C–C ₉ H ₆ N)] ₂	240, 308	362, 412
[Et ₂ Ga(O ₂ C–C ₉ H ₆ N)] ₂	240, 310	364, 412
[Me ₂ In(O ₂ C–C ₉ H ₆ N)] ₂	240, 308	356, 412
[Me ₂ GaO(C ₆ H ₄)CH = NCH ₂ –] ₂	412	462
[Et ₂ GaO(C ₆ H ₄)CH = NCH ₂ –] ₂	335	485
[Et ₂ GaO(C ₆ H ₄)CMe = NCH ₂ –] ₂	355	485
[(Me ₂ GaO–(C ₆ H ₄)CH = N–CH ₂ –CH ₂ –) ₃ N]	380	455
[(Et ₂ GaO–(C ₆ H ₄)CH = N–CH ₂ –CH ₂ –) ₃ N]	368	456
[(Me ₂ GaO–(C ₆ H ₃ OMe-3)CH = N–CH ₂ –CH ₂ –) ₃ N]	395	505
[(Et ₂ GaO–(C ₆ H ₃ OMe-3)CH = N–CH ₂ –CH ₂ –) ₃ N]	400	505

moisture hydrolysed the complex with the cleavage of N–CH₂ linkage rather than Ga–O or Ga–C bond and a new hetero-bridged complex, [{Me₂Ga}₂(μ -OH)(μ -dmpz)] (figure 4) was formed.²⁴

The complexes devoid of 'M₂(μ -O)₂' core have been synthesised by employing salen type ligands. Thus, reactions of trialkylmetal etherate with salenH₂ and saltrenH₃ yield bi- and tri-nuclear complexes (figures 5, 6).^{25,26} The salen complex represents the first example of distortion isomerism as the complex could be crystallized in orthorhombic (from benzene–hexane mixture) and monoclinic (from dichloromethane) forms. In both the forms gallium atoms are five-coordinated.

2.4 Photophysical properties

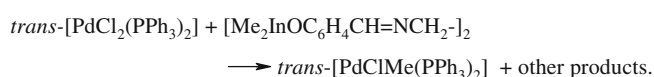
8-Hydroxyquinolate (Ox) and azomethine coordinated complexes of aluminium have been employed as organic light-emitting diodes (OLEDs).^{8,27,28} Organo-metallic complexes with chelating ligands have attracted considerable attention as promising candidates for OLED applications. Several of diorgano-gallium and indium complexes described here are emissive in fluid state at room temperature (table 1). The observed absorptions and emissions in these complexes have been attributed to transitions localised on the ligands.

2.5 C–C coupling reactions

Mononuclear organoindium complexes have been employed in cross coupling reactions of arylhalides in the presence of palladium complexes as catalyst.⁴ Thus binuclear salen complexes, which are akin to mononuclear derivatives, have been used in cross coupling reactions. 1-Bromonaphthalene is readily methylated to 1-methylnaphthalene in the presence of PdCl₂(PPh₃)₂ as catalyst. It has been shown that PdCl₂(PPh₃)₂ is converted to trans-PdMeCl(PPh₃)₂ when treated with dimethylindium complexes (scheme 6).²⁵

3. Conclusions

A variety of 1, 1-dithiolate complexes of gallium and indium have been synthesized. These are discrete monomers acquiring distorted geometries due to small bite of dithio ligands. The indium dithiolate complexes are versatile molecular precursors for the preparation of β -In₂S₃ nanoparticles. Diorgano-gallium and indium complexes with oxo ligands have been obtained conveniently by the reactions of R₃M·OEt₂ with ionic oxo ligands. The salen complexes show distortion isomerism. These complexes are emissive in solution and are employed in C–C coupling reactions in the presence of a palladium catalyst.

**Scheme 6.**

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