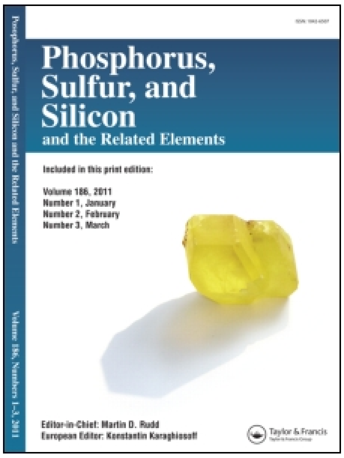

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Synthesis and Characterization of Lewis Base Stabilized Gallium-Tellurium Complexes

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Synthesis and Characterization of Lewis Base Stabilized Gallium–Tellurium Complexes

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Complexes of gallium bound to chalcogen elements recently have found importance in synthesis and as single molecular precursors for preparing thin films of gallium chalcogenides for their applications as photo-receivers for visible and near IR region. Herein we report the synthesis and characterization of some Lewis base (LB) stabilized gallium-telluride complexes. Gallium tellurolate complexes of formula, $[LB]\cdot[Ga(TePh)_3]_x$, *[*$x = 1$*, LB = 4-dimethylaminopyridine;* $x = 2$*, LB = 4,4′-methylene bis(N,N′-dimethylaniline] were prepared by reacting the corresponding Lewis base adduct of gallium(III) iodide and phenyllithium tellurolate. The complexes have been characterized by elemental analyses, ICP-MS, multinuclear NMR, and thermal and mass spectrometry. Such complexes may be potential single-molecular precursors for III–VI electronic materials.*

Keywords Gallium-tellurium complexes; lithium tellurolate; single molecular precursors

INTRODUCTION

The chemistry of gallium(III) halides and their organochalcogen complexes have recently attracted interest because of their potential applications in synthesis,[1–3] medicine[4,5] and as molecular precursors to group 13–16 materials.[6–8] Thin films of group 13–16 materials are potential alternative to group 12–16 materials for optoelectronics and photovoltaic devices[9] and as passivating layers for group 13–15 devices.[9] Although most of the work on these compounds describes thiolate and

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selenolate complexes of group 13,[11–18] not much work has been reported on tellurolato complexes.[16,17,19–23]

Our recent work on alkyls of tellurium, gallium,[24] and single source precursors for cadmium telluride[25] prompted us to attempt the synthesis of complexes with gallium–tellurium bond. In this communication, we report the synthesis and characterization of Lewis base stabilized gallium–tellurium complexes formed by the reaction of phenyllithium tellurolate, with Lewis base stabilized gallium(III) iodide.

RESULTS AND DISCUSSION

Gallium(III) iodide diethyletherate, $Et_2O{\cdot}GaI_3$, was prepared by the reaction of gallium metal with 3 equivalent of iodine in diethylether medium (Eq. (1)). The complete consumption of the metal and simultaneous discoloration of iodine indicated the formation of the diethyletherate adduct of gallium(III) iodide. The addition of diethylether solution of Lewis base to $Et_2O{\cdot}GaI_3$, formed Lewis base adducts of gallium(III) iodide immediately in yields ranging from 97–98% (Eq. (2)).

$$\mathrm{Ga} + 3/2\,\mathrm{I_2} \xrightarrow[\mathrm{Ar,\,RT}]{\mathrm{Et_2O}} \mathrm{GaI_3{\cdot}OEt_2} \qquad (1)$$

$$\mathrm{GaI_3{\cdot}OEt_2} \xrightarrow[\mathrm{Ar,\,0^\circ C}]{\mathrm{Lewis\,Base/Et_2O}} [\mathrm{Lewis\,Base}]\cdot[\mathrm{GaI_3}]_x \qquad (2)$$

Lewis Base = 4-dimethylaminopyridine, $x = 1$ (**1**)
Lewis Base = 4,4′-methylenebis(N,N′-dimethylaniline), $x = 2$ (**2**)

The compounds **1** and **2** are hygroscopic in nature. They are slightly soluble in pentane and hexane, fairly soluble in aromatic solvents and fully soluble in methanol and tetrahydrofuran (THF). These adducts have been used in further reactions without further purification. The Lewis base stabilized gallium(III) iodide adducts are more stable than gallium(III) iodide and its etherate adduct, making them potential candidates for the preparation of a variety of group 15 and 16 complexes.

Diphenylditelluride was prepared through Grignard route following the published procedure[26] (Eq. (3))

$$\mathrm{PhBr} \xrightarrow[\mathrm{(ii)\,Te}]{\mathrm{(i)\,Mg/THF}} \mathrm{PhTeMgBr} \xrightarrow[\mathrm{NH_4Cl/H_2O}]{[\mathrm{O}]} \mathrm{PhTeTePh} \qquad (3)$$

The lewis base stabilized gallium tellurium complexes (3, 4) were prepared by the reaction of phenyllithium tellurolate with corresponding gallium(III) iodide adduct (Eqs. (4), (5)).

$$\mathrm{Ph_2Te_2} + 2\,\mathrm{LiBHEt_3} \xrightarrow[-20^\circ\mathrm{C}]{\mathrm{THF}} 2\mathrm{PhTeLi} + 2\,\mathrm{BEt_3} + \mathrm{H_2} \qquad (4)$$

$$[\text{Lewis Base}] \cdot [\mathrm{GaI_3}]_x \xrightarrow[-20^\circ\mathrm{C}]{\mathrm{PhTeLi/THF}} [\text{Lewis Base}] \cdot [\mathrm{Ga(TePh)_3}]_x \qquad (5)$$

Lewis Base = 4-dimethylaminopyridine, $x = 1$ (**3**)
Lewis Base = 4,4′-methylenebis(N,N′-dimethylaniline), $x = 2$ (**4**)

A solution of phenyllithium tellurolato obtained by the reaction of diphenylditelluride was added to the solution of lewis base adducts of gallium(III) iodide. The products were extracted in toluene and dried. The complexes **3** and **4** are air stable and are soluble in toluene, THF, and methanol.

The elemental (C, H, and N) analysis data of compounds **1–4** are in agreement with the calculated values. The results of the NMR spectroscopy of these compounds are summarized in Table I.

There was a considerable upfield ^{1}H NMR shift observed for the methyl proton of dimethylamino group after complexation with phenyltellurolate. The chemical shift value of the methyl proton on dimethylamino group are observed to be in the order, free Lewis base < gallium – tellurium complex < gallium(III) iodide adducts. The complex patterns observed for **3** and **4** in the aromatic region can be attributed to merging of the chemical shifts of phenyltellurolato moiety with the aromatic proton of lewis base.

The TGA results of the compounds **3** and **4** are summarized in Table II.

TABLE I Physical and Analytical Data of Compounds 1–4

Compounds[a]	Yield (%)	m.p. (°C)[b]	^{1}H NMR δ ppm
$\mathrm{Me_2N(C_5H_4N).GaI_3}$ **1**	98	130	4.8 (s, 6H, $\mathrm{NMe_2}$), 6.9, 8.2 (d, 44, H aryl)
$\mathrm{[(CH_3)_2NC_6H_4]_2CH_2.[GaI_3]_2}$ **2**	97	180	2.5 (s, 2H, $\mathrm{-CH_2-}$), 4.2 (s, 12H, $\mathrm{NMe_2}$), 8, 8.3 (d, 8H, H aryl)
$\mathrm{Me_2N(C_5H_4N).Ga(TePh)_3}$ **3**	89	120–125 (decomp.)	3.6 (s, 6H, $\mathrm{NMe_2}$), 7.4–7.6, 7.9 (m, 19H, H aryl)
$\mathrm{[(CH_3)_2NC_6H_4]_2CH_2.[Ga(TePh)_3]_2}$ **4**	85	130–135 (decomp.)	2.9 (s, 2H, $\mathrm{-CH_2-}$), 3.6 (s, 12H, $\mathrm{NMe_2}$), 6.7–7.7 (m, 38H, H aryl)

[a] Satisfactory elemental analysis.
[b] Uncorrected.

TABLE II TGA Analysis of Data of Gallium–Tellurium Complexes

Compound	IDT (°C)[a]	FDT (°C)[b]	D_{max} (°C)[c]
3	175	350	248
	600	800	
4	170	320	222

[a] IDT; Initial decomposition temperature.
[b] FDT; Final decomposition temperature.
[c] D_{max}; Maximum decomposition temperature.

The major fragments observed in the FAB mass spectra for compounds **3** and **4** are as follows:

Compound 3:

$(CH_3)_2N(C_5H_4N)\cdot Ga(TeC_6H_5)_3$
m/e = 805
$(C_5H_4N)\cdot Ga(TeC_6H_5)_3$
m/e = 767
$Ga(TeC_6H_5)_3$
m/e = 685
$Ga(TeC_6H_5)_2$
m/e = 480
$GaTeC_6H_5$
m/e = 275

Compound 4:

$[(CH_3)_2NC_6H_4]_2CH_2\cdot[Ga(TeC_6H_5)_3]_2$
m/e = 1613
$[(CH_3)_2NC_6H_4]_2CH_2\cdot Ga(TeC_6H_5)_3$
m/e = 939
$[(CH_3)_2NC_6H_4]_2CH_2\cdot GaTe\,C_6H_5$
m/e = 460
$Ga(TeC_6H_5)_3$
m/e = 685
$Ga(TeC_6H_5)_2$
m/e = 480
$GaTe\,C_6H_5$
m/e = 275

The FAB–MS analysis confirms that the complexes are monomeric. The adduction of strong Lewis bases, i.e., 4-dimethylaminopyridine and 4,4′-methylenebis(N,N′-dimethyl)aniline, coupled with phenyl group of phenyl tellurolato moiety prevents the formation of coordinate polymers due to steric hindrance and produces monomeric complexes.

The above preliminary studies on Lewis base stabilized gallium–tellurium complexes reveal that the complexes can be considered as potential single-molecular precursors for preparing gallium telluride.

EXPERIMENTAL SECTION

All the reactions were carried out under argon using standard vacuum line technique. Solvents were carefully purified by standard procedures.[24] Boiling points and melting points are uncorrected. Phenyl bromide, 4,4′-methylenebis(N,N′-dimethylaniline),4-dimethylaminopyridine, iodine (E–Merck, Germany), lithium triethylborohydride (ACROS) were used as received. Diphenylditelluride are synthesized and purified following the published procedure.[26] Tellurium metal (5N) and gallium metal (5N) were obtained from N. F. C. Hyderabad, India. ^{1}H and ^{13}C NMR spectra were obtained from either 300 MHz Varian VXR 3005 spectrometer or Bruker 400 MHz spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal standard. FAB–MS spectra were recorded on JEOL SX/DA – 6000 mass spectrometer/data system using Argon (6 kV, 10 mA) as the FAB gas. Thermogravimetric analyses of the samples were carried out under argon atmosphere using TGA VS IA Du Pont 2100 analyzer at a heating rate of 20 K min^{-1}. Multi-elemental analysis was done using inductively coupled plasma mass spectrometer (ICP – MS), Thermo elemental VG PQ Excel.

Preparations

4-Dimethylaminopyridine. Gallium(III) Iodide (1)

A mixture of gallium (1.39 g, 20 mmol) and iodine (7.58 g, 30 mmol) in diethylether (250 mL) was stirred vigorously at room temperature in oxygen-free argon atmosphere until it became colorless. To this solution ($Et_2O{\cdot}GaI_3$), 4-dimethylaminopyridine (2.53 g, 20 mmol) in benzene (50 mL) was added dropwise with constant stirring at 0°C. A white solid immediately formed, which was washed with diethylether and vacuum dried. (Yield: 11.18 g, 98%), m.p. $>$ 130°C (decomp.) (Found, %: C, 13.9; H, 2.1; 4.6 N, calc. %: C, 14.6; H, 1.76; N, 4.8) ^{1}H NMR (400 MHz., δ ppm, $CDCl_3$, TMS): 4.8 (s, 6H, NMe_2), 6.9, 8.2 (d, 44, H aryl).

Hexaiodo-μ-[4,4′-Methylenebis(N,N′-dimethylaniline)]-digallium (2)

A solution of 4,4′-methylenebis(N,N′-dimethylaniline) (2.54 g, 10 mmol) in diethylether (50 mL) was added dropwise with constant stirring at 0°C to the solution of $Et_2O{\cdot}GaI_3$ prepared as described above. A pale green solid formed immediately, which was washed with diethylether and vacuum dried. (Yield: 11.14 g, 97%), m.p. $>$ 180°C (decomp.) (Found %: C, 15.7; H, 2.0; N, 2.0; calc.%: C, 14.45, H, 1.57; N, 1.98.) ^{1}H NMR (400 MHz, δ ppm, $CDCl_3$, TMS): 2.5 (s, 2H, $-CH_2-$), 3.6 (s, 12H, Nme_2), 8 & 8.3 (d, 8H, H aryl).

4-Dimethylaminopyridine. Tris(phenyl telluro)gallium (3)

Super hydride, $LiBHEt_3$ (7.18 mL of 1.0 M solution in THF, 7.18 mmol) was added to a solution of diphenylditelluride (1.44 g, 3.5 m mol) in THF (50 mL) dropwise at −20°C with constant stirring. The colorless solution, (PhTeLi), was added dropwise with stirring to a solution of **1** (0.67 g, 1.17 mmol) in THF (25 mL) via canula. The resulting solution was stirred for 5 h at room temperature and THF was removed under reduced pressure. The solid product was extracted with toluene, filtered, and the filtrate was concentrated to yield a colorless solid product. (Yield: 0.67 g, 72%), m.p. $>$ 120°C (decomp.) (Found %: C, 36.9; H, 3.4; N, 3.1. calc. %: C, 37.2; H, 3.1; N, 3.4.) ^{1}H NMR (400 MHz, δ ppm, CD_3OD, TMS): 4.2 (s, 6H, NMe_2), 7.4–7.6, 7.9 (m, 19H, H aryl).

Hexakis(Phenyl telluro)-μ-[4,4′-methylenebis(N,N′-dimethylaniline)]digallium (4)

The colorless solution of phenyllithium tellurolate (PhTeLi) prepared as above from diphenylditelluride (1.01 g, 2.49 m mol) in THF (25 mL) and $LiBHEt_3$ (5.1 mL of 1.0 M solution in THF, 5.1 mmol) was added to a stirred solution of **2** (1.17 g, 0.83 mmol) in THF (25 mL) following the above procedure. The resulting solution was stirred for 5 hr at room temperature and THF was removed under reduced pressure. The brownish viscous liquid obtained was treated with toluene, filtered and the filterate was concentrated to yield a brown solid. (Yield: 0.96 g, 85%), m.p. $>$ 130°C (decomp.) (Found %: C, 39; H, 3.3; N, 1.9. calc. %: C, 39.4; H, 3.2; N, 1.7) ^{1}H NMR (400 MHz, δ ppm, CD_3OD, TMS): 2.9 (s, 2H, $-CH_2-$), 3.6 (s, 12H, NMe_2), 6.7–7.7 (m, 38H, H aryl).

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