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Synthesis and application of monomeric chalcogenolates of 13 group elements

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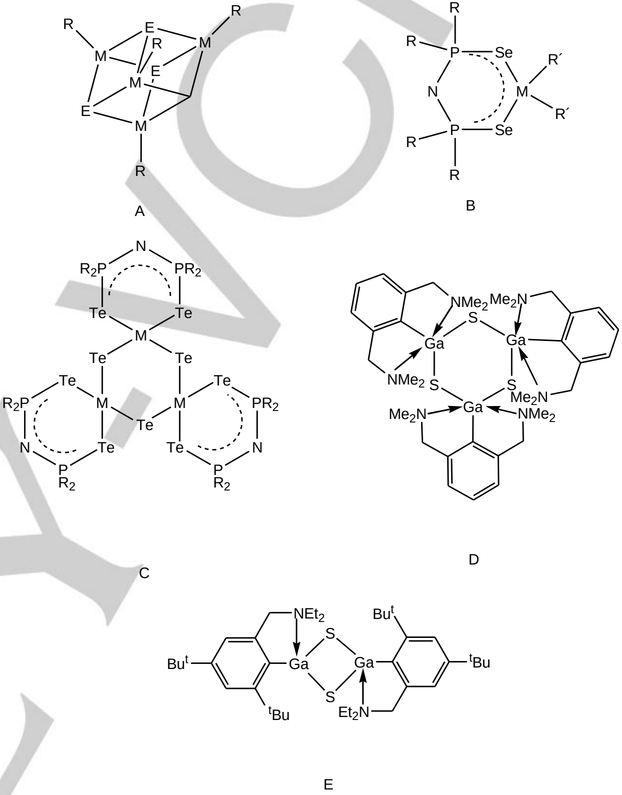
Abstract: The utilization of the N,C,N-chelating ligand L (L = {2,6-($Me_2NCH_2)_2C_6H_3\}^-$) in the chemistry of 13 group elements provided either N→In coordinated monomeric chalcogenides LIn(μ-E_4) (E = S, Se) with unprecedented InE_4 inorganic ring or monomeric chalcogenolates $LM(EPh)_2$ (M = Ga, In). Complex $LGa(SePh)_2$ has been selected as the most suitable single source precursor (SSP) for the deposition of amorphous semiconducting GaSe thin film using spin coating method.

Introduction

Due to their outstanding properties, the applications of amorphous chalcogenides of III-VI materials cover different fields such as infrared optics, photonics, development of next generation computer memories, emerging applications in medicine or military fields, etc.[1] Apart from physical vapor deposition techniques, recent synthetic approaches of these materials are based on chemical vapor deposition (CVD) of single source precursors (SSPs). Suitable SSPs are therefore widely studied and chalcogenides or chalcogenolates of group 13 elements are the most popular. Gallium and indium chalcogenides [RM(μ-E)]$_4$ (M = Ga, In; E = S, Se, Te; R = *t*Bu, CMe_2Et) were successfully applied as the prominent SSPs for III-VI materials depositions (Scheme 1A).[2] Later on, complexes [$Me_2M(SePiPr_2)_2N$][3] (Scheme 1B) and {M(μ-Te)[N(*i*$Pr_2PTe)_2$]}$_3$[4] (Scheme 1C) were used for the deposition of cubic M_2E_3 (E = Se, Te) thin films and the complexes $GaCl_3$·(*n*Bu_2E) were applied in low pressure CVD (LP-CVD) of crystalline Ga_2E_3.[5] Our previous studies also showed that N→Ga coordinated chalcogenides [LGa(μ-S)]$_3$ and [L^1Ga(μ-Se)]$_2$ (L = {2,6-$(Me_2NCH_2)_2C_6H_3\}^-$ and L^1= {2-(Et_2NCH_2)-4,6-tBu_2-$C_6H_2\}^-$) (Scheme 1D, E) can be exploited as SSPs for the deposition of III-VI amorphous thin films by spin coating method.[6,7]



Scheme 1. Examples of gallium and indium chalcogenides.

Despite these examples, chalcogenolates of group 13 elements were also used as suitable SSPs. Studies of Nomura et al. and Barron et al. demonstrated that dimeric complexes [$R_2M(ER')$]$_2$ and [$RM(ER')_2$]$_2$ (E = Ga, In; E = S, Se, Te; R = *n*Bu, *i*Bu, *t*Bu, CMe_2Et; R´= *i*Pr, *n*Pr, *t*Bu, Ph) are useful SSPs for the preparation of both ME and M_2E_3 thin films by either low pressure-CVD (LP-CVD) or CVD.[8-13] In addition, the cubic and hexagonal In_2Se_3 thin films were deposited onto Si or GaAs substrates from polymeric $In(SePh)_3$ by metal-organic CVD (MOCVD) or from In[SeC($SiMe_3)_3$]$_3$ by MOCVD, respectively.[14,15] Later on, Dutta[16] et al. reported the synthesis of Ga_2S_3 and In_2S_3 nanoparticles by thermally induced destruction of [MeM(SCH_2CH_2S)]n (M= Ga, In), that had been shown as suitable SSP despite its polymeric nature. The above mentioned polymers are also suitable starting compounds for the synthesis of [$(R_3P)_mCu_nMe_{2-x}Ga(EPh)_{n+x+1}$] (R = Me, Et, *i*Pr, *t*Bu; E = S, Se, Te; x = 0, 1) that were used as SSPs for the preparation of ternary $CuGaE_2$ semiconductors.[17] However, all these studies also revealed that synthesis of monomeric chalcogenolates of group 13 elements is rather problematic. The Lewis acidic metal centrum is usually involved

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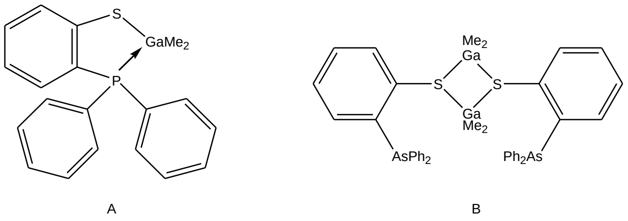
in intermolecular E→M interactions, which provide their polymeric structures making these compounds low volatile and hardly soluble in common organic solvents, therefore unfavorable for SSPs. In 1984, Hofmann[18] et al. showed that simple addition of external Lewis base NMe_3 to the polymeric gallium thiolates $Ga(SR)_3$ (R = CH_3, C_2H_5, *n*Pr, *i*Pr, Ph, CH_2Ph) provides the monomeric complexes $Ga(SR)_3{\cdot}NMe_3$. Later on, the concept of intramolecular P→Ga interaction stabilized monomeric complex $Me_2Ga\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}$ (Scheme 2A).[19] Importantly, the crucial role of Y→Ga interaction for the stabilization of monomeric chalcogenolates was also established, since the modification of donor atom Y yielded As→Ga coordinated dimeric compound $[Me_2Ga\{(\mu^2\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa S\}]_2$ (Scheme 2B).[19] Therefore, the concept and strength of Y→M intermolecular coordination can be used for the synthesis of monomeric chalcogenolates of 13 group elements.



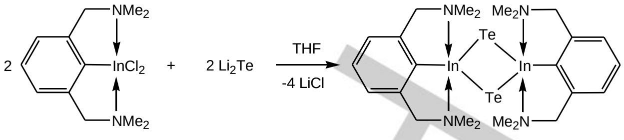
Scheme 2. Examples of gallium complexes with different coordination geometry.

As mentioned above, we have used the concept of N→Ga coordination and prepared useful SSPs $[LGa(\mu\text{-}S)]_3$ and $[L^1Ga(\mu\text{-}Se)]_2$ for deposition of GaE thin layers.[6,7] Here, we expanded our studies and showed that the N,C,N-chelating ligand L is useful for stabilization of either N→In coordinated monomeric chalcogenides $LIn(\mu\text{-}E_4)$ (E = S, Se) with unprecedented InE_4 inorganic ring or N→M monomeric chalcogenolates $LM(EPh)_2$ (M = Ga, In). All prepared compounds were characterized by means of NMR and thermogravimetric analysis (TG). Selected complexes were studied by X-ray structure analysis. Moreover, monomeric complex $LGa(SePh)_2$ has been also selected as the most suitable SSP for the deposition of amorphous semiconducting GaSe thin film using easy and low cost spin coating method .

Results and Discussion

Synthesis and characterization of N→In coordinated monomeric chalcogenides

Our initial studies were focused on the reaction of $LInCl_2$ with Li_2E (E = S, Se) in the aim to prepare N→In coordinated indium chalcogenides $[LIn(\mu\text{-}E)_2]$. However, these reaction provided ill soluble material only and interestingly, the only isolable product $[LIn(\mu\text{-}Te)]_2$ (**1**) has been obtained from the reaction of $LInCl_2$ with Li_2Te (generated *in situ* by the reaction of 2 eq. $Li[Et_3BH]$ + 1eq. Te, Scheme 3).



1

Scheme 3. Preparation of **1**

Single crystals of **1** were obtained upon storage in toluene at room temperature. The molecular structure of **1** is shown in Figure 1 and selected bond lengths and angles are given in Table 1.

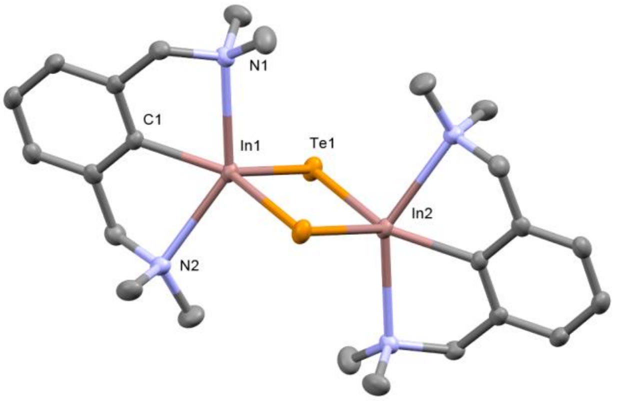


Figure 1. ORTEP plot of the crystal structure of **1** with ellipsoids drawn at 30% probability level (hydrogen atoms omitted for clarity).

The molecular structure of **1** revealed a dimeric nature with a central four-membered In_2Te_2 core. The In1 atom is five coordinated by N1, N2 and C1 atoms of the L ligand, and by two tellurium atoms. The coordination geometry can be best described as a distorted tetragonal-pyramid with $\tau = 0.09$. The C1, N1, N2 and Te1 atoms form the square base while the Te1a atom is in apical position. Both In1–N1 (2.597(3) Å) and In1–N2 (2.632(3) Å) bond distances suggest the presence of N→In coordination in **1** (compare with $\sum_{covSB}$(N, In) = 2.13 Å)[21,22]. The In–Te distances in **1** (the range of 2.7461(4) – 2.7732(3) Å) are similar with In-Te distances in $\{In(\mu\text{-}Te)[N(iPr_2PTe)_2]\}_3$ (2.744(1) and 2.8089(9))[20] and shorter than those found in tetrameric $[RIn(\mu\text{-}Te)]_4$ (R = *t*Bu, Me_2EtC), where the range of 2.87 – 2.90 Å has been obtained.[23]

The ^1H NMR spectrum of **1** showed non-equivalence of methylene CH_2N groups resonating as the AB spin system at δ 2.99 and the singlet resonance at δ 3.26 ppm. Non-equivalence of CH_2N groups was also observed in ^{13}C NMR spectrum, where signals at δ 64.2 and 64.8 ppm were observed.

The low solubility, however, defer us to study **1** as a potential SSP for InTe deposition. The change of the stoichiometry of $LInCl_2$ with E yielded monomeric N→In coordinated organoindium tetrachalcogenides $LIn(\kappa^2\text{-}E_4)$ (E= S(**2**), Se(**3**)). Thus the reaction of $LInCl_2$ with one equivalent of Li_2E_4 (generated *in situ* by the

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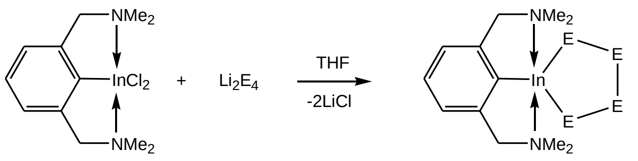
reaction of 2 eq. Li[Et_3BH] + 4 eq. E, see Scheme 4) provided well soluble complexes **2** and **3** in reasonable yields (64% for **2** and 49% for **3**).



2 (E= S), **3** (E= Se)

Scheme 4. Preparation of **2** and **3**

Single crystals suitable for X-ray diffraction analysis of **2** and **3** were obtained from saturated toluene solutions at 4°C. The molecular structures of **2** and **3** are shown in Figure 2 and selected bond lengths and angles are given in Table 1.

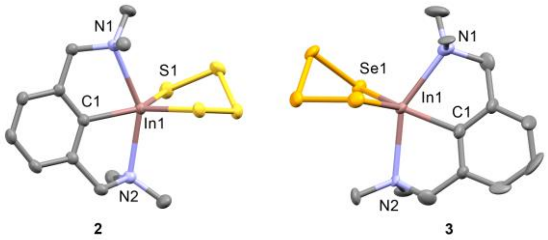


Figure 2. ORTEP plot of the crystal structure of **2** and **3** with ellipsoids drawn at 30% probability level (hydrogen atoms omitted for clarity)

Crystallographic data are summarized in Table S1. In the solid state, compounds **2** and **3** are monomeric. Both contain InE_4 (E = S, Se) five-membered ring. The In1 atoms are five-coordinated by two nitrogen and carbon atoms of the ligand L and by two E atoms of the (κ^2-E_4) fragment. The coordination geometry is a distorted trigonal-bipyramid with the C1, E1, and E4 atoms located in the equatorial positions, while both N1 and N2 atoms are in axial positions with N1–In1–N2 bond angle of 149.12(6)° (**2**) and 148.3(6)° (**3**), respectively. Nitrogen atoms are involved in N→In coordination in both compounds as demonstrated by the In–N bond lengths with the range of 2.470(1) – 2.520(2) Å (see Table 1). The bond distances In1–S1 (2.4583(6) Å) and In1–S4 (2.4535(9) Å) in **2** as well as the In1–Se1 (2.569(3) Å) and In1–Se4 (2.576(3) Å) in **3** corresponds to typical In–E covalent bonds (compare with $\sum_{covSB}$(S, In) = 2.13 Å and $\sum_{covSB}$(Se, In) = 2.58)[21,22]. It is evident that the presence of ligand L provided efficient stabilization of rare inorganic In(κ^2-E_4) ring. This five membered ring has been observed in inorganic indium polyselenides $[In_2(\kappa\text{-}Se_4)_4(\mu\text{-}Se_5)]_4^-$ or $[In(\kappa\text{-}Se_4)(m\text{-}Se)]_2$[24] and also in [Tm*t*Bu]In(κ^2-S_4) (Tm*t*Bu = tris(2-mercapto-1-tert-butylimidazolyl)borate)[25] as the closest analogues of **2** and **3**. Despite the monomeric nature of In(κ^2-E_4), close inspection in the structure of **3** revealed the presence of Se-Se´ short contacts (Figure 3). Three Se atoms of $InSe_4$ cycle are involved in the Se-Se short contacts with additional different molecules of **3** providing thus 3D polymeric arrangement of **3**. The Se-Se´ distances are in the range of 3.483 – 3.800 Å being longer than the sum of covalent radii ($\sum_{cov}$(Se,Se) = 2.32 Å)[21,22] but still shorter than sum of the Van der Waals radii of Se atoms ($\sum_{VdW}$(Se,Se) = 3.80 Å).[26] No such short contacts were found in complex **2**.

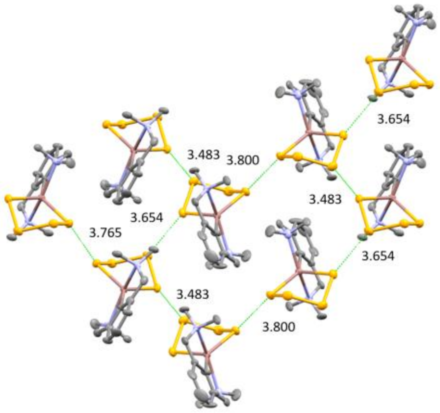


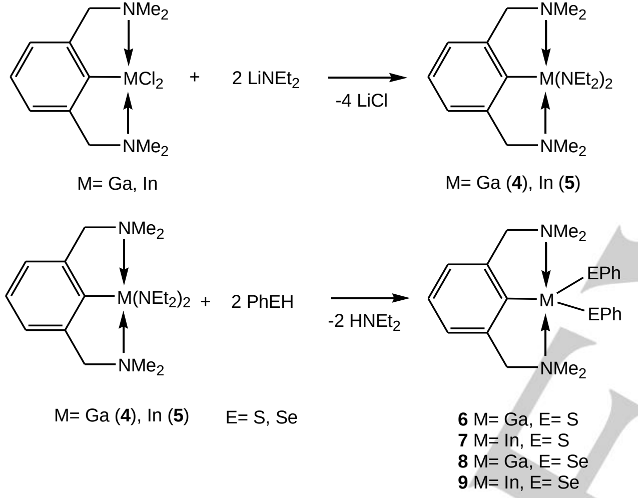
Figure 3 ORTEP plot of the crystal structure with contacts Se-Se of **3** with ellipsoids drawn at 30% probability level (hydrogen atoms omitted for clarity)

In the ^{1}H and ^{13}C NMR spectra of **2** and **3**, one set of signals was found. The ^{1}H NMR spectra revealed singlets of methyl N(CH_3)$_2$ group at δ 2.00 ppm for both compounds and methylene CH_2N group resonate at δ 2.93 ppm for **2** and at δ 3.00 ppm for **3**, respectively. In the ^{77}Se NMR spectrum of **3,** only one broad signal at δ 108.4 ppm was found suggesting fast rotation within the $InSe_4$ ring in the solution. UV-VIS absorption spectra of **2** and **3** showed absorption maximum at 237 nm (**2**) and 236 nm (**3**) due to the presence of an aromatic region and the absorption at 350 nm of $InSe_4$ ring of **3** was observed as well (for details see SI). These unique compounds with stoichiometry InE_4 were studied as potential SSPs. Unfortunately, while compound **2** is stable in propylamine, complex **3** easily eliminates elemental Se which can be the result of the existence of Se-Se contacts in **3**. The TG analysis of **2** showed the multistep decomposition (Figure S23 in SI). Due to these facts, both **2** and **3** were not studied as potential SSP. It is evident, that the presence of N→In coordination may provide monomeric organoindium chalcogenides with unusual InE_4 inorganic ring, but these compounds are not suitable SSPs for InE thin layers depositions.

Synthesis and characterization of N→M monomeric chalcogenolates LM(EPh)$_2$

As mentioned above, the chalcogenolates of 13 group elements are second category of widely studied SSPs. Since it was shown that the presence of Y→M coordination can be used for the synthesis of monomeric forms,[19] we set out to synthesize monomeric chalcogenolates by using of ligand L. We have found out an easy concept for the synthesis of desired monomeric chalcogenolates LM(EPh)$_2$ *via* two step reaction.

Starting from LMCl$_2$ (M = Ga, In),[27, 28] the organogallium and indium amides LM(NEt$_2$)$_2$ (M = Ga(**4**), In(**5**)) were prepared as oily products, by the treating of LMCl$_2$ with 2 eq. of LiNEt$_2$ (Scheme 5). Both compounds were characterized by NMR spectroscopy. Most importantly, the ^{1}H NMR spectrum showed singlet of the methylene *CH$_2$*N groups resonating at *δ* 3.34 ppm for **4** and at *δ* 3.23 ppm for **5**, respectively, while N*Et* groups resonated as a triplet (NCH$_2$*CH$_3$*) and quartet (N*CH$_2$*CH$_3$) resonances in expected ratios. Complexes **4** and **5** were found as suitable starting materials for the synthesis of monomeric chalcogenolates LM(EPh)$_2$ via an easy amine elimination reaction. Thus the treatment of with **4** and **5** with commercial available phenylthiol or selenol PhEH (E = S, Se) yielded complexes with the formula LM(EPh)$_2$ **6** – **9** (for E = S, M = Ga (**6**), M = In (**7**), for E = Se, M = Ga (**8**), M = In (**9**)) along with amine HNEt$_2$ elimination in excellent yields (up to 93%).



Scheme 5. The synthetic approach for the synthesis of monomeric chalcogenolates LM(EPh)$_2$

Complexes **6** – **9** were characterized by the help of NMR spectroscopy and X-ray structure analysis. Single crystals of **6** – **9** suitable for X-ray diffraction analysis were obtained from saturated toluene-hexane solutions at 4°C. The molecular structures of **6** – **9** showed their monomeric nature and they are depicted in Figure 4, while selected bond lengths and angles are given in Table 1.

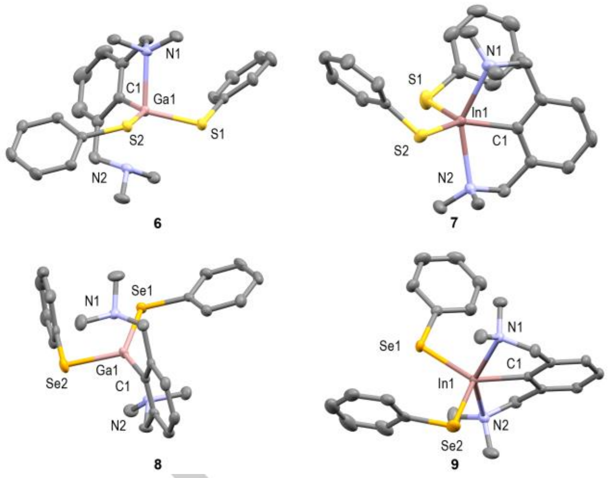


Figure 4 ORTEP plot of the crystal structure of **6** – **9** with ellipsoids drawn at 30% probability level (hydrogen atoms omitted for clarity)

The Ga and In atoms are five-coordinated by two nitrogen and carbon atoms of the ligand L and by two E atoms (E = S, Se) of the EPh fragments. The coordination geometries may be best described as distorted trigonal bipyramid with the C1, E1 and E2 in equatorial plane, while N1 and N2 atoms are in axial positions with the range of N1–M1–N2 147.3(1) – 153.94(6)°. The M–N bond distances (the range of 2.294(2) – 2.566(2) Å) suggest the presence of N→M intramolecular interaction, while M–E bond distances correlates with the sum of the covalent radii of the parent atoms ($\sum_{covSB}$(Ga,S) = 2.27 Å , $\sum_{covSB}$(Ga,Se) = 2.40 Å, $\sum_{covSB}$(In,S) = 2.45 Å and $\sum_{covSB}$(In,Se) = 2.58 Å).[21,22] In addition, the Ga1–S bond lengths (2.2517(5) and 2.2503(4) Å) in **6** are somewhat shorter that those found in monomeric P→Ga coordinated organogallium thiolates (the range of 2.268(3) – 2.343(1) Å)[19]. Similarly, the Ga1-Se bond distances (2.3735(3) and 2.3880(3) Å) in **8** are shorter than those found in the monomeric complex [(Mes)$_2$Ga(SeMes)]•(NC$_5$H$_4$-4-Me) (Mes 2,4,6-Me$_3$C$_6$H$_2$) (2.4383(9) Å).[29] Monomeric organoindium chalcogenolates were not reported so far, and the In-E bond distances found in **7** and **9** (see Table 1) are shorter than those found in dimeric or polymeric indium chalcogenolates, where the range of 2.5755 – 2.777 Å was found.[10a,30] As stated, chalcogenolates of 13 group elements easily form polymeric structures due the additional intermolecular M←E´ coordination. For example, the structures of [R´$_2$In(ER)]$_n$ contain strong intermolecular interaction In←E´ with In-E´ distances ranging from 2.6041 to 2.9007 Å.[30] No intermolecular contacts were observed in the **6** – **9** proving strictly monomeric character of these compounds.

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Table 1 Selected bond lengths (Å) and angles (deg) for **1**, **2**, **3**, **6**, **7**, **8** and **9**

	1 M=In, E= Te	2 M=In, E= S	3 M=In, E= Se	6 M=Ga, E=S	7 M=In, E=S	8 M=Ga,E=Se	9 M=In, E=Se
M1-C1	2.156(4)	2.115(2)	2.12(3)	1.941(2)	2.124(5)	1.949(2)	2.130(2)
M1-N1	2.597(3)	2.479(2)	2.47(1)	2.294(2)	2.555(3)	2.352(2)	2.520(2)
M1-N2	2.632(3)	2.520(2)	2.50(2)	2.556(2)	2.508(2)	2.547(2)	2.556(2)
M1-E1	2.7461(4)	2.4583(6)	2.569(3)	2.2517(5)	2.439(2)	2.3735(3)	2.5381(3)
M1-E2	2.7732(4)	-	-	2.2503(4)	2.446(1)	2.3880(3)	2.5533(3)
M1-E4	-	2.4535(9)	2.576(3)	-	-	-	-
N1-M1-N2	80.21(1)	149.12(6)	148.3(6)	154.80(5)	147.3(1)	153.94(6)	147.48(6)
C1-M1-E1	122.01(8)	128.38(6)	134.1(7)	129.01(5)	124.9(1)	135.68(6)	134.77(6)
C1-M1-E2	137.97(8)	-	-	131.94(5)	123.9(1)	117.38(6)	118.95(6)
C1-M1-E4	-	131.54(6)	119.8(7)	-	-	-	-
C1-M1-N1	71.72(10)	74.80(7)	74.6(8)	79.95(6)	73.0(1)	77.00(7)	74.22(7)
E1-M1-E2				98.35(2)	110.82(5)	106.89(1)	106.26(1)

The NMR spectra were consistent with their monomeric structure and one set of signals was found in the ^{1}H and ^{13}C NMR spectra of **6** – **9**. The ^{1}H NMR spectra showed singlets of methyl $N(CH_3)_2$ groups at δ 2.20 (**6**), 2.10 (**7**), 2.22 (**8**) and 2.11 (**9**) ppm and singlet resonances of methylene CH_2N protons at δ 3.13 (**6**), 3.04 (**7**), 3.10 (**8**) and 3.03 (**9**) ppm, respectively. In the ^{77}Se NMR spectra of **8** and **9**, the signals at δ 459.5 (**8**) and 2.5 (**9**) ppm were found and fall into the broad range observed for organometallic selenolates.[31] However, the signals of **8** (459.5 ppm) and of **9** (2.5 ppm) are shifted downfield in comparison to related complexes $[t\text{Bu}_2\text{Ga}(\mu\text{-Se}t\text{Bu})]_2$ (156 ppm)[10b] and $\text{Mes}_2\text{In}(\mu\text{-SeR})$ (R = Me, Ph, Mes) (range from -56 to -160 ppm)[31,32] having the SeR bridging groups. This may be the consequence of monomeric nature **8** and **9**. UV-VIS absorption spectra of **8** and **9** showed absorption maximum of aromatic part at 238 nm (**8**) and 239 nm (**9**) and shoulder at 325 nm for **8** (for details see SI).

Deposition of amorphous chalcogenide thin films by spin coating method

Monomeric complexes **6** – **9** were further studied as potential SSPs. TG analyses of **6** and **7** showed two steps decomposition (see Figures S24 – 25 in SI) starting at 190°C (for **6**) and 150° (for **7**) and continue until 340°C (for **6**) and 315° (for **7**). Moreover, the observed mass losses (69% for **6** and 62% for **7**) in comparison with expected (79% for **6** and 72% for **7**) indicate incomplete decomposition of **6** and **7**. In contrast, the TG analysis of **8** and **9** showed one step decompositions (see Figures S26 – 27 in SI) and continue until 295°C (for **8**) and 255°C (for **9**). The total expected (73% for **8** and 69% for **9**) and observed (70% for **8** and 66% for **9**) mass losses indicate the formation of GaSe and InSe material after complete decomposition of SSPs. Therefore both compounds **8** and **9** were tested as suitable SSPs for preparation of GaSe and InSe thin films by spin coating method. Due to monomeric nature of **8** and **9**, compounds are highly soluble in propylamine (about 300 mg in 1 ml propylamine) and thus the concentrations up to 0.5 mol/l may be obtained. In comparison, amorphous GaSe thin films have been recently obtained from 0.06 mol/l propylamine solution of N→Ga coordinated organogallium selenides.[7] The use of highly concentrated propylamine solution of **8** (c = 0.5 mol/l) led to the preparation of GaSe thin films with poor quality by spin coating. Therefore, the propylamine solution of **8** with c = 0.087 mol.l^{-1} was used for the preparation of GaSe thin films by spin coating on silicon substrate using 1000 and 1500 rpm. Prepared GaSe thin films were amorphous, as confirmed by XRD (SI Figure 1) and showed strong influence of thickness on spinning speed (Table S2 in SI). Although the composition has been similar in both experiments, the better results were obtained for deposition at 1500 rpm. The scanning electron microscopy (SEM) (Fig. 5a) and atomic force microscopy (AFM) (Fig. 5b) images showed that spin-coated films have higher surface roughness (AFM root mean square roughness <4 nm within 2 μm x 2 μm scan area) in comparison with thin amorphous chalcogenide films fabricated by physical vapor deposition techniques.

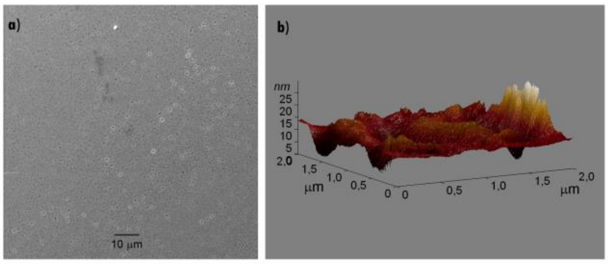

Figure 5 a) SEM image, b) AFM image of the surface of 1500 rpm spin-coated GaSe thin film fabricated using of **8** SSP.

Energy-dispersive X-ray spectroscopy (EDX) revealed that the chemical composition of the resulting thin film is $Ga_{49.6}Se_{50.4}$ for 1500 rpm. The Ga/Se atoms ratio in **8** is therefore retained in the prepared GaSe thin films. Optical functions of prepared GaSe layer as well as their thickness were obtained from the analysis of variable angle spectroscopic ellipsometry (VASE) data. The thickness of the as-dried Ga-Se thin film was 83.7±2 nm and the refractive index was n = 2.28 at λ = 1.5 μm (Figure 6). These values are little bit lower, but comparable to those found for amorphous GaSe thin films produced by vacuum evaporation (n ≈ 2.41 at λ = 1.6 μm) noting that the chemical composition of the latter was probably richer in selenium content due to the fact that $GaSe_9$ starting material was used.[33] Refractive index data obtained in this work are in agreement with our previous report (n = 1.96 - 2.26 at λ = 1.5 μm).[7] Finally, compound **9** was used as SSPs for the preparation of InSe thin films by spin-coating method on silicon substrate using 1000 and 1500 rpm. Both propylamine solutions of **9** with c = 0.09 and 0.5 mol.l^{-1} were tested, but the resulting thin films, after the annealing, contained 25−35 at.% of Se according to EDX.

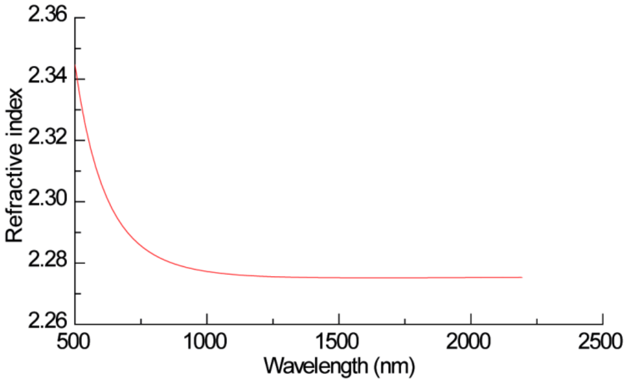

Figure 6 Typical dispersion of the refractive index of spin-coated Ga-Se thin film (1500 rpm).

Conclusions

In conclusion, we have shown that the utilization of the N,C,N-chelating ligand L in the chemistry of 13 group elements may provide N→In coordinated monomeric chalcogenides $LIn(\mu\text{-}E_4)$ (E = S, Se) with unprecedented InE_4 inorganic ring. Despite interesting ratio of In : E (1 : 4), these compounds were not successfully applied as SSPs for the deposition of InE thin layers. The concept of N→M coordination was applied for the synthesis of monomeric chalcogenolates $LM(EPh)_2$ **6** – **9** (M = Ga, In, E = S, Se). The isolation of organogallium and indium amides $LM(NEt_2)_2$ (M = Ga(**4**), In(**5**)) enabled synthesis of **6** – **9** *via* an easy amine elimination reaction by the treatment of **4** and **5** with commercial available phenylthiol or selenol PhEH. This method may be very useful for the synthesis of various monomeric chalcogenolates of 13 group elements. All compounds **6** – **9** were characterized by the help of NMR spectroscopy, X-ray diffraction and TG analysis.

As the consequence of monomeric character of **8**, propylamine solution of **8** with the concentrations up to 0.5 mol/l may be obtained. Based on these result, complex **8** has been selected as the most suitable SSP for the deposition of amorphous semiconducting GaSe thin films using spin coating method. The GaSe thin films were characterized by SEM-EDX (topography, chemical composition), VASE (film thickness, refractive index) and AFM (surface roughness) and obtained data showed that the semiconducting GaSe material prepared by spin coating method from **8** is comparable with those prepared by vacuum evaporation.

Experimental Section

Supporting Information. Experimental details, NMR spectra for prepared complexes, crystallographic parameters, (CCDC nos. 1915933-1915939 for **1**, **2**·$0.5C_6H_6$, **3** and **6** – **9**, respectively), Variable Angle Spectroscopic Ellipsometry (VASE), thermogravimetric analyses and UV-VIS measurements.

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Keywords: single-source precursor • spin-coating • GaSe material • amorphous thin films • chalcogenolates

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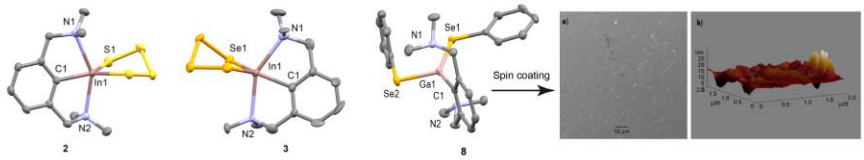

Synthesis of indium chalcogenides with In_2Te_2, InS_4 or $InSe_4$ rings and monomeric chalcogenolates $LM(EPh)_2$ (L = $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}^-$, M = Ga, In, E = S, Se) is shown. $LGa(SePh)_2$ compound has been successfully applied for amorphous GaSe thin film preparation.

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Synthesis and application of monomeric chalcogenolates of 13 group elements