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New Heterobimetallic and Polymeric Selenocarboxylates Derived from $[M(SeC\{O\}Ph)_4]^-$ ($M = Ga$ and In) as Molecular Precursors for Ternary Selenides

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$(Et_3NH)[In(SeC\{O\}Ph)_4]\cdot H_2O$ (**1**) along with heterobimetallic and polymeric metal selenocarboxylates, namely $[NaGa(SeC\{O\}Ph)_4]$ (**2**), $[K(MeCN)_2Ga(SeC\{O\}Ph)_4]$ (**3**), $[NaIn(SeC\{O\}Ph)_4]$ (**4**), $[K(MeCN)_2In(SeC\{O\}Ph)_4]$ (**5**), $[(Ph_3P)_2CuIn(SeC\{O\}Ph)_4]\cdot CH_2Cl_2$ (**6**), and $[(Ph_3P)_2AgIn(SeC\{O\}Ph)_4]\cdot CH_2Cl_2$ (**7**), have been synthesized by incorporating either alkali metal ions (Na^+ and K^+) or group 11 metal ions (Cu(I) and Ag(I)) into the $[M(SeC\{O\}Ph)_4]^-$ anion. Crystal structures determined by X-ray crystallography indicate that **3** and **5** have one-dimensional coordination polymeric structures while **6** and **7** have an $M(\mu\text{-}Se)_2In$ ($M = Cu$, Ag) core. The thermal decomposition of these compounds except **4** lead to the formation of the corresponding metal selenides as confirmed by thermogravimetric analysis and in some cases by powder X-ray diffraction studies.

Introduction

Over the years, there has been sustained interest in the development of the chemistry of metal thiocarboxylate complexes, stemming not only from their interesting structural chemistry[1−4] but also from the fact that many of them can be used as single molecular precursors for the low-temperature synthesis of metal sulfide materials, thin films, and nanoparticles.[5−8] In contrast to metal thiocarboxylate complexes, little is known about the chemistry of metal selenocarboxylate complexes to date. A major impediment to the development of this chemistry has been the difficulty in synthesizing the metal selenocarboxylates along with the air- and moisture-sensitive nature of monoselenocarboxylate anions, $RC\{O\}Se^-$. However, Kato et al. have developed synthetic routes to alkali metal selenocarboxylates and paved way to the growth of metal selenocarboxylates.[9] Our recent work revealed that the chemistry of monoselenocarboxylate anions need not be similar to that of the monothiocarboxylates,[10,11] as has been observed between the thiolates and selenolates.[12] Due to our sustained interest in the chemistry of metal thio- and selenocarboxylates, in general, we are prompted to explore the synthesis of $[In(Se\{O\}Ph)_4]^-$ and $[Ga(SeC\{O\}Ph)_4]^-$ anions and to use them as metalloligands to bind to various metal ions. Here, we report the syntheses and structures of $(Et_3NH)[In(SeC\{O\}Ph)_4]\cdot H_2O$ and one-dimensional coordination polymeric compounds $[A(MeCN)_xM$-

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$(SeC\{O\}Ph)_4]$ (A = Na, K; M = In, Ga; x = 0, 2). Further, we have also successfully synthesized and characterized two heterobimetallic selenocarboxylates of Cu(I) and Ag(I), namely, $[(Ph_3P)_2M'In(SeC\{O\}Ph)_4]\cdot CH_2Cl_2$ (M′ = Cu, Ag). Recently we reported that the metal selenocarboxylates can be used as single precursors for metal selenides.[10,13] Therefore, we have also examined the feasibility of using these metal selenocarboxylates to prepare $AMSe_2$ materials.

Experimental Section

All reactions were performed under an atmosphere of argon using Schlenk techniques. All the starting materials were obtained commercially and were used as received except benzoyl chloride, which was purified by distillation under N_2. Gallium metal salt $Ga(NO_3)_3\cdot xH_2O$ ($x \approx 3$ by thermogravimetric analysis)[14] was obtained from Sigma-Aldrich. Acetonitrile was distilled from calcium hydride under N_2. Na_2Se and K_2Se were prepared by the literature method.[15] ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker ACF300 NMR spectrometer, with chemical shifts referenced to residual nondeuterated solvent and external H_3PO_4, respectively. Mass spectra were obtained with a Finnigan MAT LCQ (ESI) spectrometer. All elemental analyses were performed by the Microanalytical Laboratory in NUS. Thermogravimetric analysis (TGA) was recorded on an SDT 2960 with simultaneous differential thermal analysis (DTA)−TGA. Approximately 10 mg of the precursor was decomposed under inert N_2 flow (90 mL/min), and a heating rate of 10 $deg\cdot min^{-1}$ was used. Powder X-ray diffraction (XRPD) patterns were recorded on a Siemens D5005 X-ray powder diffractometer with Cu Kα radiation (40 kV, 40 mA). Each sample was measured at the rate of 0.01 deg/s from 20° to 80°.

Sodium Selenocarboxylate, $Na^+PhC\{O\}Se^-$.[9a] Benzoyl chloride (1.05 mL, 9.05 mmol) was added to a suspension of Na_2Se (1.47 g, 11.77 mmol) in MeCN at 0 °C under an argon atmosphere, and the color of the mixture rapidly changed to yellow. After the mixture was stirred for 1 h, NaCl and unreacted Na_2Se were filtered off using a G4 Umkehr filter. The solution of $Na^+RC\{O\}Se^-$ was used in the following syntheses of compounds **2** and **4**.

Potassium Selenocarboxylate, $K^+PhC\{O\}Se^-$.[9b] The reaction was carried out similarly to that for sodium selenocarboxylate, but K_2Se was used instead of Na_2Se. The solution of $K^+RC\{O\}Se^-$ was used in the following syntheses of compounds **3** and **5**.

$(Et_3NH)[In(SeC\{O\}Ph)_4]\cdot H_2O$, 1. To a solution of $[NaIn(SeC\{O\}Ph)_4]$ (0.18 g, 0.20 mmol) (refer to the synthesis of **4**) in acetone (4 mL), Et_3NHCl (0.03 g, 0.20 mmol) dissolved in MeCN (4 mL) was added dropwise at ambient condition. The solution was allowed to stir for 0.5 h and the solvents were removed completely under vacuum. The product was then extracted in CH_2Cl_2 (5 mL) and layered with hexane. A crystalline product was obtained by keeping the solution at 5 °C overnight. The yellow crystals were filtered off, washed with MeOH and Et_2O, and then dried under vacuum and stored at 5 °C for further use. Yield: 0.15 g (78%). Elemental Anal. Calcd for $InSe_4O_4C_{34}H_{36}N\cdot H_2O$ (mol wt. 971.34): C, 42.04; H, 3.94; N, 1.44%. Found: C, 41.82; H, 3.95; N, 1.47%. ^1H NMR ($CDCl_3$) δ_H: 8.01 (8H, d, J = 6 Hz, ortho-proton), 7.31 (8H, t, J = 7.5 Hz, meta-proton), 7.45 (4H, t, J = 7.5 Hz , para-proton), 3.33 (6H, q, J = 8 Hz, $\underline{CH_2}CH_3$), 1.31 (9H, t, J = 7.5 Hz, $CH_2\underline{CH_3}$). ^{13}C NMR ($CDCl_3$) δ_c: for selenobenzoate ligand: 126.92 ($C_{2/6}$ or $C_{3/5}$), 128.31 ($C_{2/6}$ or $C_{3/5}$), 130.05 (C_4), 140.94 (C_1), 201.15 ($\underline{C}OSe$). ESI-MS (m/z) (CH_2Cl_2) at 50 °C: 853.1 ($[In(SeC\{O\}Ph)_4]^-$, 60%); 1058.5 ($[In(SeC\{O\}Ph)_4]^- + 2Et_3N$, 60%); 391.4 ($[Na(SeC\{O\}Ph)_2]^-$, 18%); 185.5 ($PhC\{O\}Se^-$, 100%). TG weight loss for one H_2O: expected, 1.9%; found, 1.8%.

$[NaGa(SeC\{O\}Ph)_4]$, 2. The solvent from the sodium selenocarboxylate solution prepared as described above was removed to dryness under vacuum. Deaerated H_2O (30 mL) was then added to the crude sodium monoselenocarboxylate and the insoluble precipitate was filtered off. $Ga(NO_3)_3\cdot 3H_2O$ (0.70 g, 2.26 mmol) dissolved in deaerated H_2O (10 mL) was added dropwise to the yellow filtrate via a dropping funnel to get a pale yellow precipitate. The contents were allowed to stir for 1.5 h in ice-cold condition. The white precipitate was filtered off, washed with plenty of water, and then dried under vacuum and stored at 5 °C. Yield: 0.67 g (50%). Elemental Anal. Calcd for $NaGaSe_4C_{28}H_{20}O_4$ (mol wt 829.02): C, 40.57; H, 2.43; Na, 2.77%. Found: C, 40.53; H, 3.00; Na, 3.21%. ^1H NMR (d_6-acetone) δ_H: 8.00 (8H, d, J = 7 Hz, ortho-proton), 7.40 (8H, t, J = 6 Hz, meta-proton), 7.51 (4H, t, J = 6 Hz para-proton). ^{13}C NMR (d_6-acetone) δ_c: for selenobenzoate ligand: 126.12 ($C_{2/6}$ or $C_{3/5}$), 128.61 ($C_{2/6}$ or $C_{3/5}$), 131.05 (C_4), 142.94 (C_1), 201.50 ($\underline{C}OSe$). ESI-MS (m/z) (acetone) at 50 °C: 806.9 ($[Ga(SeC\{O\}Ph)_4]^-$, 100%); 884.9 ($[Ga(SeC\{O\}Ph)_4]^- + (CH_3)_2CO + H_2O$, 12%); 1635 ($[(Ga(SeC\{O\}Ph)_4)_2Na]^-$, 45%); 185.2 ($PhC\{O\}Se^-$, 100%).

$[K(MeCN)_2Ga(SeC\{O\}Ph)_4]$, 3. To the MeCN solution (25 mL) of $K^+PhC\{O\}Se^-$ (3.33 mmol), $Ga(NO_3)_3\cdot 3H_2O$ (0.19 g, 0.62 mmol) in MeOH (5 mL) was added to get a yellow precipitate. The contents were then stirred for 1.5 h and heated in a water bath to dissolve the yellow precipitate. The insoluble KNO_3 was filtered off and the yellow solution was left at 5 °C overnight to obtain yellow needle-like crystals, which was then filtered, washed with a small amount of cold EtOH and Et_2O, and dried in vacuum. A second crop was obtained by slowly removing the solvent under vacuum. Total yield: 0.09 g (16%). Anal. Calcd for $KGaSe_4C_{28}H_{20}O_4\cdot MeCN$ (mol wt 886.18): C, 40.66; H, 2.62; K, 4.41%. Found: C, 40.07; H, 2.19; K, 4.63%. The analysis of the dried sample matched with only one MeCN, while fresh single crystal used for X-ray crystallography has two MeCN molecules. ^1H NMR (d_6-acetone) δ_H: 8.01 (8H, d, J = 6 Hz, ortho-proton), 7.40 (8H, t, J = 6 Hz, meta-proton), 7.51 (4H, t, J = 7.5 Hz, para-proton). ^{13}C NMR (d_6-acetone) δ_c: for selenobenzoate ligand: 127.25 ($C_{2/6}$ or $C_{3/5}$), 128.61 ($C_{2/6}$ or $C_{3/5}$), 131.25 (C_4), 142.97 (C_1), 200.80 ($\underline{C}OSe$). ESI-MS (m/z) (acetone) at 50 °C: 807.0 ($[Ga(SeC\{O\}Ph)_4]^-$, 100%); 1029.0 ($[KGa(SeC\{O\}Ph)_4 + PhCOSe^-]$, 6%); 884.9 ($[Ga(SeC\{O\}Ph)_4]^- + (CH_3)_2CO + H_2O$, 4%); 185.3 ($PhC\{O\}Se^-$, 40%). TG weight loss for one MeCN: expected, 4.6%; found, 2.7%.

$[NaIn(SeC\{O\}Ph)_4]$, 4. Compound **4** was synthesized via a synthetic strategy similar to that used for **2** except that $InCl_3$ was used instead of $Ga(NO_3)_3\cdot 3H_2O$. Yield: 1.55 g (78%). Elemental Anal: Calcd. for $NaInSe_4C_{28}H_{20}O_4$ (mol wt 874.11): C, 38.47; H, 2.31; Na, 2.63%. Found C, 38.39; H, 2.17; Na, 2.58%. ^1H NMR (d_6-acetone) δ_H: 8.02 (8H, d, J = 6 Hz, ortho-proton), 7.40 (8H, t, J = 6 Hz, meta-proton), 7.51 (4H, t, J = 6 Hz para-proton). ^{13}C NMR (d_6-acetone) δ_c: For selenobenzoate ligand: 126.12 ($C_{2/6}$ or $C_{3/5}$), 128.41 ($C_{2/6}$ or $C_{3/5}$), 130.75 (C_4), 141.94 (C_1), 201.80 ($\underline{C}OSe$). ESI-MS (m/z)(acetone) at 50 °C: 898.5, ($[NaIn(SeC\{O\}Ph)_4] + Na^+$, 100%); 852.8, ($[In(SeC\{O\}Ph)_4]^-$, 60%); 185.3, ($PhC\{O\}Se^-$, 100%).

$[K(MeCN)_2In(SeC\{O\}Ph)_4]$, 5. Compound **5** was synthesized using a procedure similar to that for **3** except that $InCl_3$ was used instead of $Ga(NO_3)_3\cdot 3H_2O$. Unlike $Ga(NO_3)_3\cdot 3H_2O$, $InCl_3$ powder was added directly into $PhCOSe^-$ solution. Yield: 70%. Anal. Calcd for the desolvated product, $KInSe_4C_{28}H_{20}O_4$ (mol wt 890.22): C,

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Table 1. Crystallographic Data and Refinement Parameters for **1**, **3**, **5**, **6**, and **7**

	1[a]	**3**	**5**	**6**	**7**
formula	$C_{34}H_{38}InNO_5Se_4$	$C_{32}H_{26}N_2GaKO_4Se_4$	$C_{32}H_{26}N_2InKO_4Se_4$	$C_{65}H_{52}CuInO_4P_2Se_4Cl_2$	$C_{65}H_{52}AgInO_4P_2Se_4Cl_2$
fw	971.34	927.21	972.31	1524.11	1568.44
T, K	223	223	233	223	223
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	13.0491(5)	12.3468(5)	12.4406(7)	12.6678(9)	12.7983(6)
b, Å	13.0760(4)	13.8322(6)	13.8078(7)	13.9765(10)	14.0942(7)
c, Å	21.7114(7)	20.7219(8)	20.7791(1)	18.8875(13)	18.7509(9)
α, deg	90	90	90	90.999(2)	91.009(1)
β, deg	90	91.535(2)	91.647(2)	101.415(2)	100.373(1)
γ, deg	90	90	90	110.784(2)	111.089(1)
V, Å^3	3704.6(2)	3537.7(3)	3567.9(3)	3050.5(4)	3091.7(3)
Z	4	4	4	2	2
ρ, g cm^{-3}	1.742	1.741	1.810	1.659	1.685
μ, mm^{-1}	4.607	5.048	4.896	3.300	3.229
final R indices[b] ($I > 2\sigma(I)$)	R1 = 0.0362, wR2 = 0.0855	R1 = 0.0346, wR2 = 0.0724	R1 = 0.0457, wR2 = 0.0776	R1 = 0.0380, wR2 = 0.0694	R1 = 0.0318, wR2 = 0.0708

[a] Flack parameter, 0.020(9). [b] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$.

37.78; H, 2.26; K, 4.39%. Found: C, 37.80; H, 2.18; K, 4.39%. The dried sample contains no MeCN solvent molecule, while fresh single crystal used for X-ray crystallography has two MeCN molecules. ^{1}H NMR (d_6-acetone) δ_H: 8.02 (8H, d, J = 6 Hz, ortho-proton), 7.41 (8H, t, J = 7.5 Hz, meta-proton), 7.52 (4H, t, J = 7.5 Hz para-proton). ^{13}C NMR (d_6-acetone) δ_c: for selenobenzoate ligand: 127.10 ($C_{2/6}$ or $C_{3/5}$), 128.48 ($C_{2/6}$ or $C_{3/5}$), 131.05 (C_4), 142.90 (C_1), 201.50 ($\underline{\text{C}}$OSe). ESI-MS (m/z) (acetone) at 50 °C: 852.8 ([In(SeC{O}Ph)$_4$]$^-$, 100%); 930.0 ([In(SeC{O}Ph)$_4$]$^-$ + $(CH_3)_2CO$ + H_2O, 2%); 1074.7 ([KIn(SeC{O}Ph)$_4$ + PhCOSe$^-$], 15%); 1742.0 ([(In(SeC{O}Ph)$_4$)$_2$K]$^-$, 80%); 185.2 (PhC{O}Se$^-$, 17%).

[(Ph$_3$P)$_2$CuIn(SeC{O}Ph)$_4$]·CH$_2$Cl$_2$, 6. Compound **6** was synthesized using a procedure similar to that for **1** except that [(Ph$_3$P)$_2$Cu(NO$_3$)][16] was used instead of Et$_3$NHCl. Yield: 78%. Elemental Anal. Calcd for $CuInSe_4P_2C_{64}H_{50}O_4\cdot CH_2Cl_2$ (mol wt 1524.18): C, 51.22; H, 3.44; P, 4.06%. Found: C, 51.56; H, 3.18; P, 4.30%. ^{1}H NMR (CDCl$_3$) δ_H: 7.88 (8H, d, J = 6 Hz, ortho-proton), 7.15 (8H, t, J = 7.5 Hz, meta-proton), 7.25−7.45 (34H, m, para-proton and PPh$_3$), 5.32 (2H, CH$_2$Cl$_2$). ^{13}C NMR (CDCl$_3$) δ_c: for selenobenzoate ligand: 126.12 ($C_{2/6}$ or $C_{3/5}$), 128.11 ($C_{2/6}$ or $C_{3/5}$), 130.75 (C_4), 141.94 (C_1), 202.50 ($\underline{\text{C}}$OSe); for PPh$_3$: 128.15 (C_3), 129.30 (C_4), 133.14 (C_1), 133.95 ($\underline{\text{C}}_2$). ^{31}P NMR (CDCl$_3$) δ_p: −1.31. ESI-MS (m/z) (CH$_2$Cl$_2$) at 50 °C: 848.7 ([(PPh$_3$)$_3$Cu]$^+$, 100%); 852.9 ([In(SeC{O}Ph)$_4$]$^-$, 100%); 185.3 (PhC{O}Se$^-$, 85%); 703.7 (In(SeC{O}Ph)$_3$ + Cl$^-$, 18%). TG weight loss for one CH$_2$Cl$_2$: expected, 5.5%; found, 3.2%. Single crystals of **6** were obtained by layering Et$_2$O over the CH$_2$Cl$_2$ solution of **6** and stored at 5 °C for overnight.

[(Ph$_3$P)$_2$AgIn(SeC{O}Ph)$_4$]·CH$_2$Cl$_2$, 7. To an acetone (5 mL) solution of [NaIn(SeC{O}Ph)$_4$] (0.64 g, 0.73 mmol) a CH$_2$Cl$_2$ (5 mL) solution of [(PPh$_3$)$_2$Ag(NO$_3$)][16] (0.51 g, 0.73 mmol) was added dropwise. A brownish gray precipitate was formed immediately upon stirring. The solution was allowed to stir for 0.5 h, and the precipitate was filtered off and washed with MeOH, H$_2$O, and Et$_2$O. The product was then dried under vacuum and stored at 5 °C. Yield: 0.71 g (65%). Elemental Anal. Calcd for $AgInSe_4P_2C_{64}H_{50}O_4\cdot CH_2Cl_2$ (mol wt 1568.51): C, 49.77; H, 3.34; P, 3.95%. Found C, 50.28; H, 3.09; P, 3.89%. ^{1}H NMR (CDCl$_3$) δ_H: 7.73 (8H, d, J = 6 Hz, ortho-proton), 7.11 (8H, t, J = 7.5 Hz, meta-proton), 7.24−7.42 (34H, m, para-proton and PPh$_3$). ^{13}C NMR (CDCl$_3$) δ_c: for selenobenzoate ligand: 127.12 ($C_{2/6}$ or $C_{3/5}$), 128.61 ($C_{2/6}$ or $C_{3/5}$), 131.05 (C_4), 142.94 (C_1), 201.50 ($\underline{\text{C}}$OSe); for PPh$_3$: 128.15 (C_3), 129.30 (C_4), 133.14 (C_1), 133.95 ($\underline{\text{C}}_2$). ^{31}P NMR (CDCl$_3$) δ_p: 7.35. ESI-MS (m/z) (CH$_2$Cl$_2$) at 50 °C: 631.0 ([(PPh$_3$)$_2$Ag]$^+$, 100%); 852.8 ([In(SeC{O}Ph)$_4$]$^-$, 100%); 185.3 (PhC{O}Se$^-$, 100%). TG weight loss for one CH$_2$Cl$_2$: expected, 5.4%; found, 2.3%. Single crystals of [(PPh$_3$)$_2$AgIn(SeC{O}Ph)$_4$] were obtained by layering Et$_2$O over CH$_2$Cl$_2$ solution of **7** at 5 °C overnight.

X-ray Crystallography. The diffraction experiments were carried out on a Bruker SMATR CCD diffractormeter with a Mo Kα sealed tube. The program SMART[17] was used for collecting frames of data, indexing reflection, and determining lattice parameters; SAINT[17] was used for integration of the intensity of reflections and scaling. SADABS[18] was used for absorption correction, and SHELXTL[19] was used for space group and structure determination and least refinement on F^2. Selected crystallographic data of experimental details are compiled in Table 1.

Results and Discussion

Synthesis. The compounds [NaGa(SeC{O}Ph)$_4$] (**2**), [K(MeCN)$_2$Ga(SeC{O}Ph)$_4$] (**3**), [NaIn(SeC{O}Ph)$_4$] (**4**), and [K(MeCN)$_2$In(SeC{O}Ph)$_4$] (**5**) were prepared by simple metathesis between the metal salts and appropriate amounts of the corresponding alkali metal selenocarboxylates in either H$_2$O or MeCN solvent. (Et$_3$NH)[In(SeC{O}Ph)$_4$]·H$_2$O (**1**), [(Ph$_3$P)$_2$CuIn(SeC{O}Ph)$_4$]·CH$_2$Cl$_2$ (**6**), and [(Ph$_3$P)$_2$AgIn(SeC{O}Ph)$_4$]·CH$_2$Cl$_2$ (**7**) were prepared by the metathesis between the ionic salts Et$_3$NHCl, [(Ph$_3$P)$_2$Cu(NO$_3$)] or [(Ph$_3$P)$_2$Ag(NO$_3$)], and **4** in either CH$_2$Cl$_2$/(Me)$_2$CO or CH$_2$Cl$_2$/MeCN solvents.

Compounds **2** and **4** could not be isolated if the reaction was conducted in MeCN alone. Similarly, complexes **1**, **6**, and **7** could not be isolated from the in situ reaction, unlike the corresponding metal thiocarboxylates, which were isolated from in situ complexation.[7,8] Unfortunately, the gallium analogues of **1**, **6**, and **7** could not be isolated from the

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(16) (a) Kubas, G. J. *Inorg. Synth.* **1970**, *19*, 93. (b) Bowmaker, G. A.; Effendy, A. H. J.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 1387.

(17) *SMART & SAINT Software Reference Manuals*, version 5.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

(18) Sheldrick, G. M. *SADABS a software for empirical absorption correction*, version 2.03; University of Göttingen: Göttingen, Germany, 2000.

(19) *SHELTX Reference Manual*, version 6.13; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

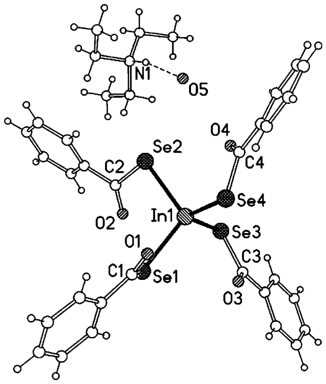

Figure 1. Ball-and-stick diagram of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**

Bond Distances	
In(1)−Se(1)	2.5615(7)
In(1)−Se(2)	2.5790(7)
In(1)−Se(3)	2.5784(7)
In(1)−Se(4)	2.5659(7)
Se(1)−C(1)	1.861(6)
Se(2)−C(2)	1.902(6)
Se(3)−C(3)	1.918(5)
Se(4)−C(4)	1.914(5)
Bond Angles	
Se(1)−In(1)−Se(2)	106.74(3)
Se(1)−In(1)−Se(3)	104.50(3)
Se(1)−In(1)−Se(4)	116.64(3)
Se(2)−In(1)−Se(3)	110.04(2)
Se(2)−In(1)−Se(4)	104.63(2)
Se(3)−In(1)−Se(4)	114.08(3)

reaction solution under these conditions due to rapid decomposition of the products even though the solution was kept at 5 °C for recrystallization.

Compounds **2**−**5** are insoluble in CH_2Cl_2 or $CHCl_3$ but soluble in Me_2CO and warm MeCN, and compounds **1**, **6**, and **7** are very soluble in CH_2Cl_2 and $CHCl_3$. The compounds are stable for months if stored at 5 °C. However, unlike the corresponding metal thiocarboxylates,[14] compounds **2**−**5** decomposed slowly upon standing in ambient condition for long time. The structural characterization of these compounds mainly depends on X-ray crystallography, because the usual spectroscopic techniques are not very informative.

Structural Descriptions. Compounds **3** and **5** are one-dimensional coordination polymers in which the $[M(SeC\{O\}Ph)_4]^-$ ions (M = Ga, In) act as a multidentate ligand bound to the K cation. In addition, the structures of **3** and **5** are isotypical. On the other hand, **1** is a discrete ionic complex. Compounds **6** and **7** are bimetallic dimers with an $A(\mu\text{-Se})_2In$ core (A = Cu, Ag) and are isostructural with each other and to the corresponding silver thiocarboxylate structure.[7] Detailed structural descriptions are given in the following sections.

Structure of $(Et_3NH)[In(SeC\{O\}Ph)_4]\cdot H_2O$, 1. **1** contains a discrete unit of $[In(SeC\{O\}Ph)_4]^-$ anions and hydrated cation as illustrated in Figure 1. Selected bond distances and angles of compound **1** are listed in Table 2. As shown in Figure 1, the indium metal center in **1** is covalently bonded to four selenocarboxylates through selenium atoms. Further, the Se−In−Se angles (104.50(3)−116.64(3)°) indicate distortions from the ideal tetrahedral geometry. In **1**, the triethylammonium cation is hydrogen bonded to the water molecule through the amine hydrogen atom. Overall, the structural feature of **1** resembles that of the corresponding thiocarboxylate.[8]

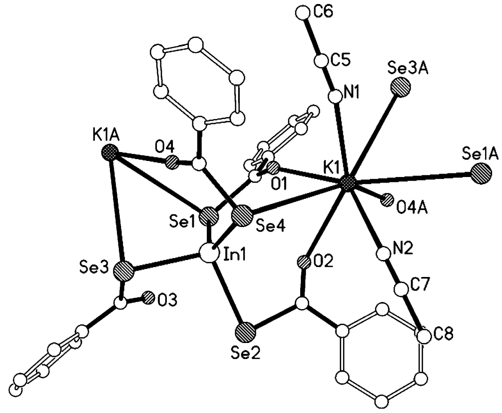

Figure 2. Perspective view showing the coordination environment around the metal centers in **5**.

Table 3. Selected Bond Distances (Å) and Angles (deg) in **3** and **5**

	3 (M = Ga)	**5** (M = In)
Bond Distances		
M−Se(1)	2.393(1)	2.560(1)
M−Se(2)	2.419(1)	2.606(1)
M−Se(3)	2.418(1)	2.610(1)
M−Se(4)	2.398(1)	2.581(1)
O(1)−K(1)	2.703(3)	2.696(4)
O(2)−K(1)	2.741(3)	2.797(4)
O(4)−K(1)[a]	2.700(3)	2.726(4)
K(1)−N(1)	2.841(4)	2.852(6)
K(1)−N(2)	2.851(5)	2.844(6)
Bond Angles		
Se(1)−M−Se(2)	110.30(2)	110.93(3)
Se(1)−M−Se(3)	106.45(2)	105.34(2)
Se(1)−M−Se(4)	123.47(2)	125.65(2)
Se(3)−M−Se(2)	103.82(2)	102.45(2)
Se(4)−M−Se(2)	105.20(2)	105.12(2)
Se(4)−M−Se(3)	105.92(2)	104.93(2)
O−K−O	69.84(8)−88.05(9)	67.9(1)−87.7(1)
N−K−Se	70.10(8)−131.10(8)	68.9(1)−133.8(1)
Se−K−Se	60.92(2)−114.23(2)	64.71(2)−142.21(4)
O−K−Se	61.27(6)−148.24(7)	62.17(8)−150.4(1)
O−K−N	74.86(1)−143.37(9)	74.5(1)−142.5(1)
N−K−N	111.8(1)	109.2(2)

[a] Symmetry transformation used to general equivalent atoms: $-x + 3/2$, $y + 1/2$, $-z + 1/2$.

Structures of $[K(MeCN)_2\{M(SeC\{O\}Ph)_4\}]$ (M = Ga (3), In(5)). As mentioned above, both **3** and **5** are isostructural. A portion of the polymeric structures of these two compounds showing the details of the geometries around the metal ions and $PhC\{O\}Se^-$ ligands is illustrated in Figure 2 for **5**. Selected bond lengths and angles are displayed in Table 3. In these two compounds, four of the selenobenzoate ligands are bonded to the metal ions through selenium atoms. The distances between gallium and selenium in **3** are nearly identical, which range from 2.393(1) to 2.419(1) Å. Unlike **3**, the In−Se distances in **5** are in a wider range, 2.560(1)−2.610(1) Å. In these structures, the M···O distances are less than the sum of their van der Waals radii (3.40 Å), suggesting the presence of weak interactions in these two complexes.[20]

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[20] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

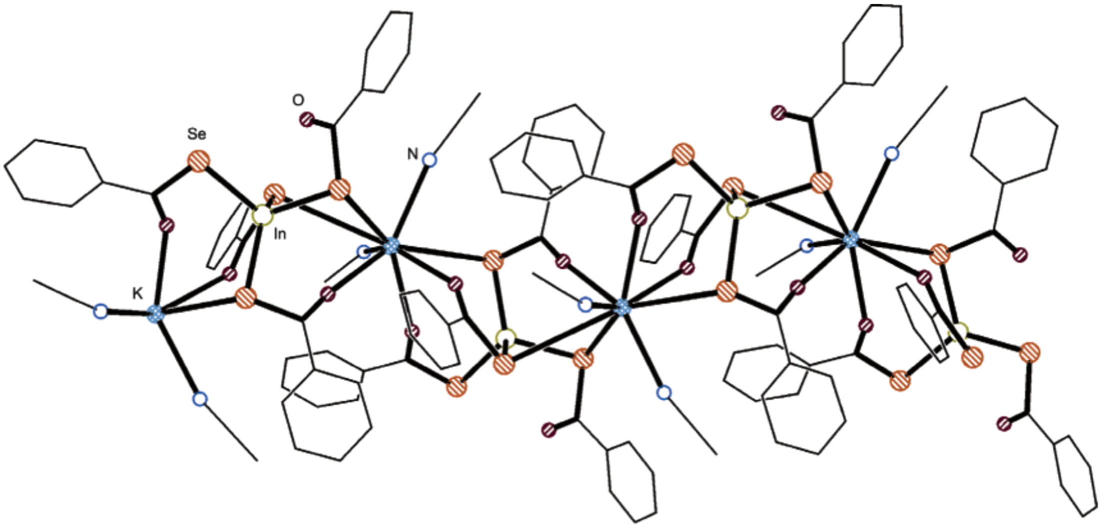

Figure 3. Segment of one-dimensional coordination of **5**. The hydrogen atoms are omitted for clarity. The color codes are as follows: blue sphere, K; red, O; orange, Se; blue open circle, N; yellow circle, In.

In the solid state **3** and **5** form one-dimensional (1D) polymeric structures with alternating repeating units of $[K(MeCN)_2]^+$ and $[M(SeC\{O\}Ph)_4]^-$. A portion of these coordination polymers is illustrated in Figure 3, and each polymeric strand is arranged parallel to the *b*-axis. One of the $[M(SeC\{O\}Ph)_4]^-$ units binds to potassium as a tridentate ligand through two carboxyl oxygen atoms, namely O(1) and O(2), and a selenium atom (Se(4)). Further, another $[M(SeC\{O\}Ph)_4]^-$ unit binds through one oxygen atom, O(4), and two selenium atoms, Se(1) and Se(3). In addition, two acetonitrile molecules coordinate to the potassium ion. The K−Se distances in **3** (3.750(1)−3.824(1) Å) and **5** (3.668(2)−3.857(2) Å) are larger than the reported values found in potassium 2-methoxybenzenecarboselenoate (3.309(1)−3.625(2) Å)[21] but shorter than the sum of van der Waals radii (4.70 Å).[20] If the weak interactions between K and Se are taken into account, the geometry at the potassium ion is considered as eight-coordinated highly distorted hexagonal bipyramidal geometry with a $Se_3O_3N_2$ donor set. Compound **5** is found to be isomorphous to $[K(MeCN)_2In(SC\{O\}Ph)_4]$,[14] but the coordination number and geometry at K are slightly different.

Structures of $[(Ph_3P)_2M'In(SeC\{O\}Ph)_4]\cdot CH_2Cl_2$, (M′ = Cu (6), Ag (7)). A perspective view of **6** and **7** is shown in Figure 4, and selected bond distances and angles are given in Table 4. In the asymmetric unit containing heterobimetallic compounds, a CH_2Cl_2 molecule is present in the crystal lattice similar to the thiocarboxylate analogue of Ag(I) compound.[7] As illustrated in Figure 4, a $[In(SeC\{O\}Ph)_4]^-$ anion is bonded to $M'(PPh_3)_2^+$ cation through two bridging $SeC\{O\}Ph^-$ ligands through Se atom forming a $M'InSe_2$ ring (M′ = Cu, Ag). Apart from four In−Se bonds, weak interactions were also observed between the indium and two carbonyl oxygens in **6** (In(1)···O(3), 2.883 Å; In(1)···O(4), 2.976 Å) and in **7** (In(1)···O(3), 2.897 Å; In(1)···O(4), 2.958 Å). Hence, the geometry at the indium metal center is six-coordinated distorted octahedron and the geometry at the group 11 metal ion is distorted tetrahedron with $P_2M'Se_2$ core (M′ = Cu, Ag). The M′−P distances are normal and do not warrant any additional comment. It may be noted that the benzoyl group at the bridging selenium atoms have “anti” configuration and the Se−C bonds are tilting away from the M′-

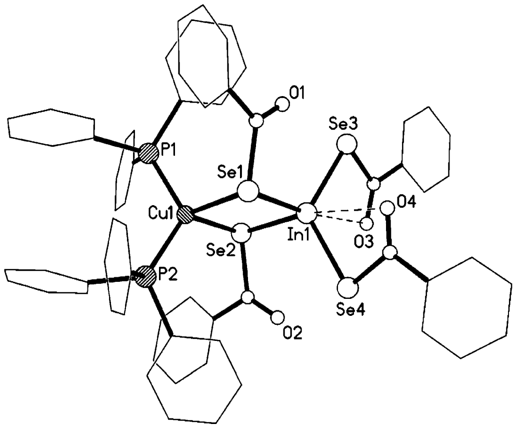

Figure 4. Perspective view of **6**. Hydrogen atoms have been removed for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of **6** and **7**

	6 (M′ = Cu)	**7** (M′ = Ag)
	Bond Distances	
In(1)−Se(1)	2.636(1)	2.637(1)
In(1)−Se(2)	2.635(1)	2.640(1)
In(1)−Se(3)	2.554(1)	2.555(1)
In(1)−Se(4)	2.551(1)	2.554(1)
M′−P(1)	2.283(1)	2.467(1)
M′−P(2)	2.278(1)	2.461(1)
M′−Se(1)	2.567(1)	2.778(1)
M′−Se(2)	2.567(1)	2.767(1)
	Bond Angles	
Se(2)−In(1)−Se(1)	93.36(2)	99.30(1)
Se(3)−In(1)−Se(1)	112.84(2)	111.47(2)
Se(4)−In(1)−Se(1)	103.63(2)	101.25(2)
Se(3)−In(1)−Se(2)	107.12(2)	103.87(1)
Se(4)−In(1)−Se(2)	110.48(2)	109.55(1)
Se(4)−In(1)−Se(3)	124.90(2)	127.95(2)
P(2)−M′−P(1)	121.77(4)	122.98(3)
Se(2)−M′−Se(1)	96.67(2)	92.99(1)
M′−Se(1)−In(1)	84.96(2)	83.76(1)
M′−Se(2)−In(1)	84.98(2)	83.92(1)

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(21) Niyomura, O.; Kato, S.; Kanda, T. *Inorg. Chem.* **1999**, *38*, 507.

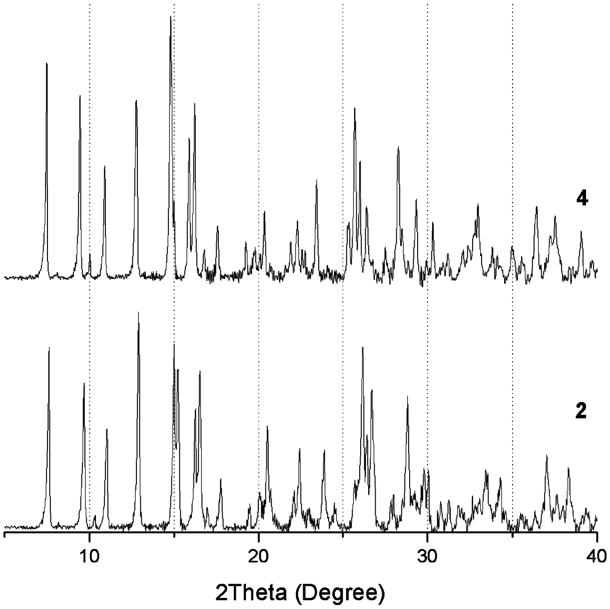

Figure 5. XRPD patterns of **2** and **4**.

$(PPh_3)_2$. The nonbonding Cu···In distance, 3.52 Å, is, therefore, longer compared to distances in the reported compounds such as $(Ph_3P)_2Cu(\mu\text{-SEt})_2In(SEt)_2$ (3.34 Å), $(Ph_3P)Cu(\mu\text{-SeEt})_2In(SeEt)_2$ (3.32 Å), and $(Ph_3P)_2Cu(\mu\text{-}(S(iso\text{-}Bu))_2In(S(iso\text{-}Bu))_2$ (3.24 Å).[22]

Overall, **6** and **7** are isostructural and isomorphous to each other. However, **7** is isostructural with the corresponding thiocarboxylate analogue, but **6** is not. This could be due to the large size of the selenium atom that is able to release the steric crowd around Cu(I), thereby accommodating one more PPh_3 unlike the sulfur analogue.[7a] This is supported by the fact that the larger size of Ag atom enables $(Ph_3P)_2$-Ag to bind to the $[In(EC\{O\}Ph)_4]^-$ (E = S, Se) units without affecting the overall molecular strength or crystal packing.[7b] A close examination of the molecular structure of **6** in Figure 4 may reveal the presence of an approximate noncrystallographic 2-fold symmetry along the M′−In bond. Interestingly, this is not reflected in the crystal structure symmetry.

The presence of alkali metal inflicts a strong distortion at the In(III) metal centers through the selenocarboxylate ligands. However, the bond parameters at the potassium cations in **3** and **5** are similar, remain undisturbed by changing from thiobenzoate to selenobenzoate ligand, and have little effect on the overall polymeric structure of this type of compound. Unfortunately, single crystals of **2** and **4** suitable for X-ray crystallography were not obtained, but the XRPD patterns of **2** and **4** are similar (Figure 5), indicating that they are isomorphous and isostructural, but different from the generated XRPD patterns of $[NaIn(SCOPh)_4]$[14] and **5**. Hence choice of solvent has a strong effect on the overall crystal structure of these alkali metal incorporated group III metal thio- or selenocarboxylates.

Thermogravimetry and Pyrolysis. The usefulness of compounds **1**−**7** as single-source precursors for metal selenide materials was investigated by thermogravimetry and pyrolysis experiments. The TGA curves are presented in Figure 6, and the results are summarized in Table 5.

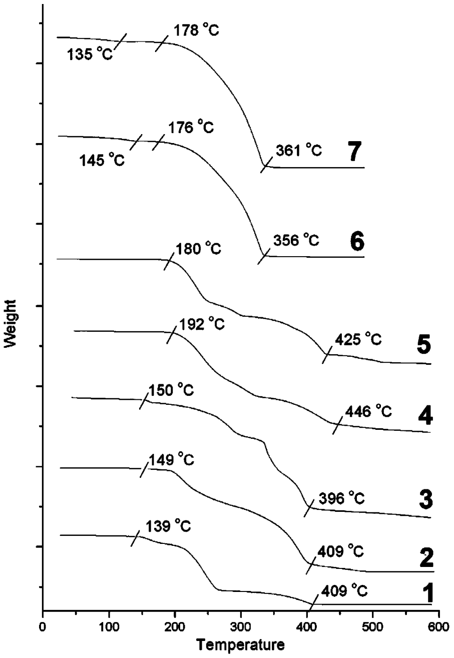

Figure 6. Overlay of thermogravimetric curves of **1**−**7**.

It is unusual that **6** and **7** can retain CH_2Cl_2 up to 145 and 135 °C, respectively, and similar behavior was also observed in the corresponding thiocarboxylates.[7a] To our surprise, no distinct intra- or intermolecular interactions that one might expect for retaining the CH_2Cl_2 molecule were found in the crystal lattices of these compounds, and we are currently investigating this unusual retention of CH_2Cl_2 solvent well above its boiling point. All the compounds started decomposing in the temperature range 144−192 °C and completed 400−450 °C, except **6** and **7**, where the decomposition process ended at a relatively low temperature. Overall, the decomposition profiles of these metal selenocarboxylates are similar to those of the corresponding metal thiocarboxylates.[7,8,14] As shown in Figure 6, no distinct plateau was observed after major weight loss in **2**−**5** until at least 600 °C. This suggested that the $AMSe_2$ (A = Na, K; M = In, Ga) could be unstable at high temperature and undergo decomposition which led to the decrease of the residual weight. In fact, we previously observed that $GaCuS_2$ is unstable at high temperature:[8a] when we tried to deposit this material at temperatures higher than 400 °C by MOCVD, it decomposed to a mixture of products. Thus, this illustrated the poor thermal stability of some ternary metal sulfides.

The pyrolysis products of **2**−**5** were stored under dry argon atmosphere to prevent any decomposition, as it has been stated that $NaInSe_2$ is unstable at ambient conditions and will react with moisture to form H_2Se and acid.[23] The elemental stochiometry of the decomposed products characterized by EDX (energy dispersive X-ray spectroscopy) are in the expected range of 1:1:2 (Na/K:Ga/In:Se) for

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(22) Hirpo, W.; Dhingra, S.; Sutorik, A. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 1597.

(23) Macintyre, J. E. *Dictionary of Inorganic Compounds*, 1st ed.; London: New York, 1992.

Table 5. Pyrolysis and TGA Results for **1**−**7**

compd	temp range (°C)	residual wt obsd (calcd) (%)	residual wt from pyrolysis[a] (%)	product of decomposition (JCPDS No.)
1	50−139	98.7 (98.2)		desolvated **1**
	139−409	25.0 (24.5)	27.1	In_2Se_3 (40-1407)
2	149−409	23.0−28.0 (30.2)	27.3	$NaGaSe_2$[b]
3	150−396	26.7−32.3 (30.1)	26.8	$KGaSe_2$ (isostructural to $KGaTe_2$ (01-070-5286)
4	192−446	32.7−38.2 (33.8)	37.3	unknown
5	180−425	26.4−36.0 (35.0)	30.0	$KInSe_2$ (01-070-6110).
6	RT−145	96.8 (94.5)		desolvated **6**
	176−356	23.9 (22.1)	22.3	$CuInSe_2$ (40-1487)
7	RT−135	97.7 (94.6)		desolvated **7**
	178−361	26.5 (24.3)	26.6	$AgInSe_2$ (035-01099)

[a] **4** was heated at 500 °C for 2 h; **1**, **2**, and **5** were heated at 450 °C for 1 h; **3** was heated at 350 °C for 30 min; **6** and **7** were heated at 300 °C for 30 min. [b] Based on the EDX analyses.

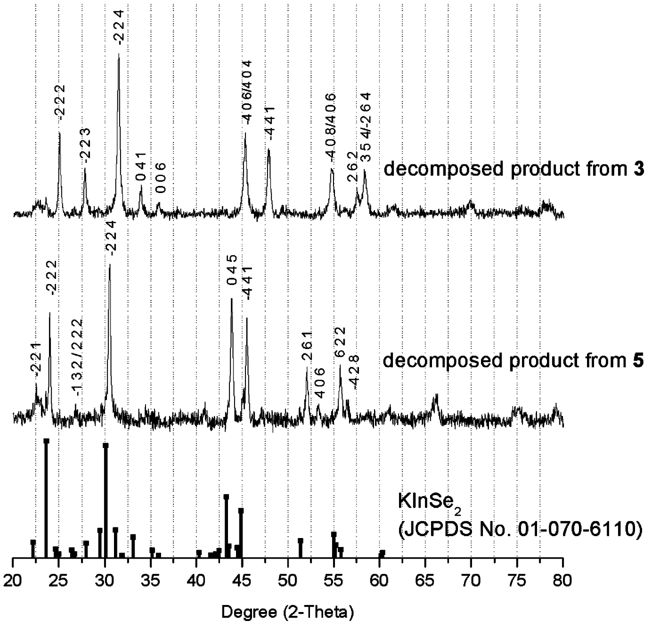

Figure 7. XRPD patterns of pyrolyzed products of **3** and **5** along with the reported XRPD pattern of $KInSe_2$.

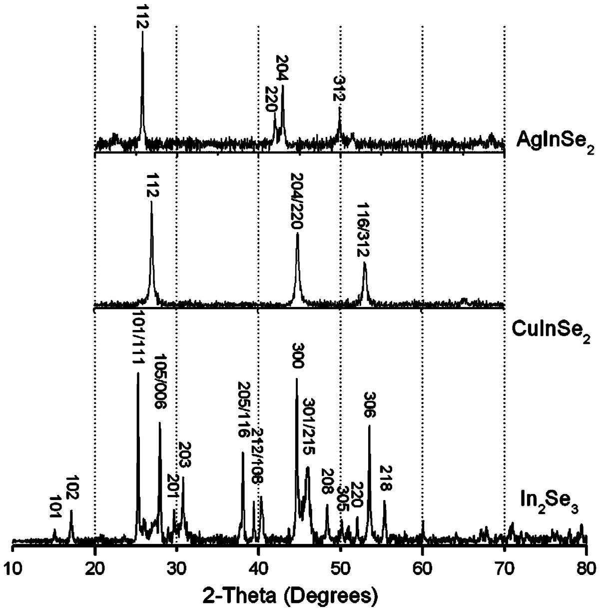

Figure 8. XRPD patterns of decomposed products of compounds **1**, **6**, and **7**.

compounds **2**, **3**, and **5**.[24] Further, the XRPD pattern of the decomposed product of **5** is matched with the known monoclinic $KInSe_2$ (JCPDS No. 01-070-6110) as shown in Figure 7. The XRPD pattern for $KGaSe_2$ is not available to date; however, the XRPD pattern of the product of pyrolysis of **3** closely resembles that of $KGaTe_2$ (JCPDS No. 01-070-5286) and hence it may be concluded that $KGaSe_2$ might be isostructural with the monoclinic $KGaTe_2$.[24] Although EDX shows the correct stoichiometry for the decomposed product of **2** to be 1:1:2 (Na:Ga:Se). The XRPD pattern of the pyrolyzed product does not match or resemble with any known phase of sodium gallium selenide including $Na_2Ga_2Se_3$.[24] Hence, based on the EDX analysis, we proposed that the XRPD pattern could be due to a new phase $NaGaSe_2$. Both the EDX and XRPD analyses of the pyrolyzed product of **4** do not match with $NaInSe_2$. Hence compound **4** might adopt a different decomposition pathway and the expected $NaInSe_2$ is not formed.

In contrast, a sharp plateau was observed in the TGA of **1**, **6**, and **7**. The observed residual weights are in fair agreement with the calculated values. XRPD patterns of the decomposed products of **1**, **6**, and **7** confirmed the formation of the corresponding ternary metal selenides as shown in Figure 8. The sharp peaks in the XRPD patterns stem from the strong crystalline nature of the metal selenides. Further, no other peaks are present at high temperatures, showing the feasibility of using these metal selenocarboxylates as single source precursors to synthesize the corresponding ternary metal selenides in either the form of thin films or nanoparticles. This is supported by the fact that **7** decomposed in the presence of dodecanethiol and oleylamine ligands when a new phase $AgInSe_2$ nanorod, which is isostructural to $AgInS_2$, can be obtained.[25]

Summary

We have shown that $[M(SeC\{O\}Ph)_4]^-$ can be used as metalloligand to bind to alkali metal ions and $[In(SeC\{O\}Ph)_4]^-$ can be used for Cu(I) and Ag(I). The solid-state structures of **6** and **7** are isotypical and are very similar to that of $[(Ph_3P)_2AgIn(SC\{O\}Ph)_4]\cdot CH_2Cl_2$.[7a] The K(I) salts of $[M(SeC\{O\}Ph)_4]^-$ (M = Ga, In) have 1D coordination

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(24) See Supporting Information.

(25) Ng, M. T.; Boothroyd, C.; Vittal, J. J. *J. Am. Chem. Soc.* **2006**, *128*, 7118.

polymeric structures in the solid state. Based on the TGA, pyrolysis, EDX, and XRPD experiments, **2**, **3**, and **5** thermally decomposed to the corresponding $AMSe_2$. If these compounds are subjected to one-pot colloidal synthesis, one might be able to isolate stable $AMSe_2$ nanoparticles by the use of surfactants to cap and stabilize them.[25,26] On the other hand, In_2Se_3, $CuInSe_2$, and $AgInSe_2$ can be obtained respectively from **1**, **6**, and **7**. Hence, these precursors may provide an alternative route to synthesizing the corresponding thin films, which are promising photovoltaic materials.

Acknowledgment. We would like to thank the NUS for their generous financial support through Grant R-143-000-283-112.

Supporting Information Available: Crystallographic data in CIF format for **1**, **3**, and **5**−**7**. EDX spectra of the pyrolysis products of **2**−**5**, and table containing the elemental analysis of the pyrolyzed products of **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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