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Chemistry of Metal Thio- and Selenocarboxylates: Precursors for Metal Sulfide/Selenide Materials, Thin Films, and Nanocrystals

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ABSTRACT
This Account focuses on recent developments of the chemistry of metal thio- and selenocarboxylates in our laboratory and potential use of some of these compounds as single-source precursors for making metal sulfide and selenide bulk materials, thin films, and nanoparticles.

Introduction

Monochalcogenocarboxylates (RC{O}E^- anion, E = S, Se, or Te) are asymmetrical ligands in which one of the oxygen atoms of the carboxylate anion is replaced by a chalcogen atom[1] and normally exist either in the form of an acid or alkali-metal salt. Historically, the synthesis of thiocarboxylic acid was first reported by Kekulé in 1854.[2a] Since then, the synthesis and properties of numerous chalcogenocarboxylic acids have been published in the literature.[2b,c] Recently, a comprehensive review by Kato highlighted the developments in the chemistry of monochalcogenocarboxylates over the last century.[2a] In contrast, until very recently little has been known about the chemistry of selenocarboxylic acid and/or the corresponding alkali-metal salts, probably due to their instability and handling difficulties associated with them.

Over the years metal sulfides and selenides, which includes powders, thin films, and nanoclusters, have generated a great deal of scientific and technological interest for a number of different reasons.[3] The semiconducting nature of these materials has led to fundamental interest in the synthesis of molecular clusters and nanocrystals to investigate size-dependent structure−property relationships. A wide variety of synthetic methods have been developed to synthesize these materials. Of these an attractive method is the single molecular source approach where the organic fragments present in the coordination metal complexes of chalcogenide- or chalcogen-containing ligands are removed and metal chalcogenides are reassembled at relatively low temperature under mild conditions.[4a,b] This is somewhat different from the *chimie douce* approach developed by Rouxel.[5] Hampden-Smith et al. have shown that the metal thiocarboxylates can be used as single molecular precursors for metal sulfide materials since they undergo thiocarboxylic anhydride elimination reaction, as shown in eqs 1 and 2, to form "MS".[6a]

$$2M(SOCR)_2L_2 \rightarrow [(RCOS)M{-}S{-}M(SOCR)]L_2 + S(COR)_2 \quad (1)$$

$$[(RCOS)M{-}S{-}M(SOCR)]L_2 \rightarrow 2MS + (RCO)_2S + 2L \quad (2)$$

Using this strategy they synthesized various group 12 metal sulfide nanoparticles using the corresponding metal thiocarboxylates precursors, $M(SC\{O\}R)_2L_2$ (M = Zn, Cd; R = alkyl, aryl; L = Lewis base).[6a] They also demonstrated that various metal sulfide thin films can be deposited using metal thiocarboxylate precursors using aerosol-assisted chemical vapor deposition (AACVD) techniques.[6b,c] Recently, Chin et al. discovered that the silver thiocarboxylate can take a different decomposition pathway to form Ag_2S in the presence of an amine in solution.[7] In this Account we discuss interesting structural chemistry of metal thio- and selenocarboxylates developed in our laboratory and how some of these compounds have been used as precursors for metal sulfides and selenides.

Group 11 Metal Thio- and Selenocarboxylates

Reactions of triphenylphosphine with copper(I) thioacetate or thiobenzoate led to formation of five different products depending on the stoichiometry of the reactants as illustrated in Scheme 1.[8] In these neutral compounds remarkable structural diversity with variable bonding modes including μ_3-S and μ_3-S_2,O were exhibited[8] along with a μ_2 bridging mode of the sulfur atom which is ubiquitous in thiolate chemistry.[9a,b] In $[Cu_4(SC\{O\}Me)_4(PPh_3)_4]$ (**1**) the Cu and S atoms are alternatively bonded to form an eight-membered Cu_4S_4 ring similar to the copper(I) thiolate tetramer, $[(SPh)_4Cu_4(PPh_3)_4]$,[9c] and two sulfur atoms further bridge two copper atoms to form a highly distorted 'stepladder' arrangement with a Cu···Cu separation of 2.7477(6) Å. Under similar experimental conditions thiobenzoate anion yielded a highly distorted cubane-like neutral cluster $[Cu_4(SC\{O\}Ph)_4(PPh_3)_3]$ (**2**). This reflects the influence of the R group of the thiocarboxylate ion on the solid-state structures. When the stoichiometric ratio of CuCl, NaSC{O}R, and PPh_3 is 1:1:

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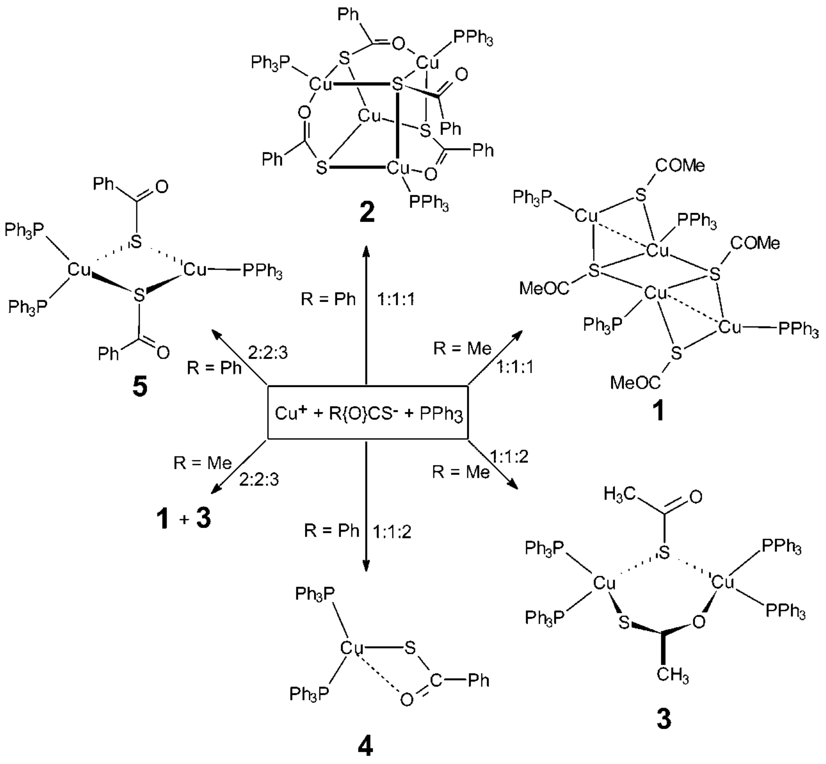
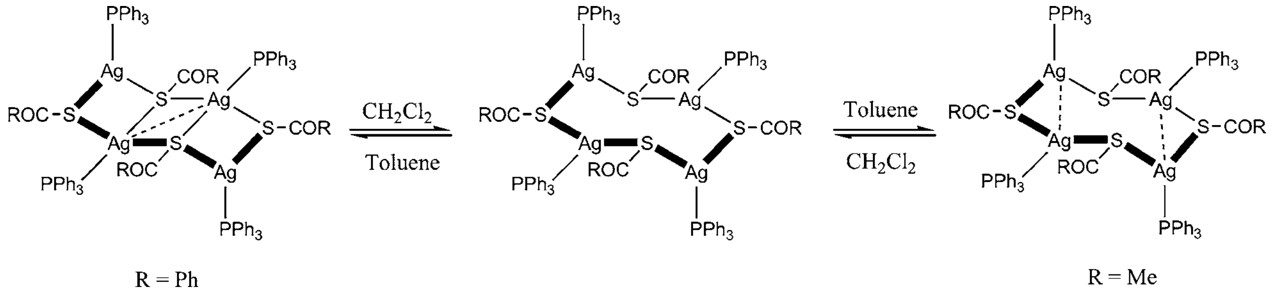
Scheme 1. Reactivity of Copper Thiocarboxylates with Triphenylphosphine



Scheme 2. Solvent-Dependent Interconversion of Deformational and Conformational Isomers of 6 (R = Ph) and 7 (R = Me)



2, thioacetate furnished a dimer **3** while thiobenzoate ligand yielded a monomer **4**. ^{31}P NMR of these triphenylphosphine copper thiocarboxylates in $CDCl_3$ and CD_2Cl_2 shows fast exchange between the phosphines and copper ions at all the temperatures studied.

On the other hand, the chemistry of the neutral triphenylphosphine adducts of silver thiocarboxylates is quite different from that of their copper analogues. Only monomeric $[Ag(SC\{O\}R)(PPh_3)_2]$ (R = Me, Ph) and tetrameric $[(AgPPh_3)_4(\mu\text{-}SC\{O\}R)_4]$ (R = Me (**6**), Ph (**7**)) have been isolated by varying the metal to ligand ratio and experimental conditions.[10] The solid-state structures of the tetramers depend on the solvents used for preparation or recrystallization as shown in Scheme 2. When crystallized from CH_2Cl_2 **6** and **7** have eight-membered Ag_4S_4 rings in the solid state. In toluene **6** forms a conformational isomer with an Ag···Ag separation of 3.1461(5) Å, whereas **7** gave a ladder structure similar to **1**. The ability of the sulfur atom in the $PhC\{O\}S^-$ ligand to form μ_2-S and μ_3-S bridging and the nature of Ag(I) to display variable coordination geometries aided formation of two deformational isomers for silver(I) thiobenzoates. The size and coordinating ability of the solvents play a role in these systems during and/or prior to nucleation. The solvent CH_2Cl_2, being smaller in size with more coordinating ability, keeps the atoms in the Ag_4S_4 ring away from each other, preventing formation of any bonds across the eight-membered rings, whereas the atoms in the Ag_4S_4 tetramer are pushed across the ring to interact with each other due to the poor coordinating ability and relatively larger size of toluene. The solvent-dependent structures are depicted in Scheme 2.

The selenocarboxylate chemistry is not necessarily similar to that of thiocarboxylate, and this indeed is found to be the case for Cu(I) and Ag(I). The unsymmetrical dimers $[(Ph_3P)_3M_2(SeC\{O\}R)_2]$ (M = Ag and Cu) were isolated irrespective of the experimental conditions employed.[11,12]

While exploring the versatile bonding ability of the thiocarboxylate ligand, the triphenylphosphine was replaced by bis(diphenylphosphino)methane (dppm), and a range of trinuclear compounds, $[M_3(\mu\text{-dppm})_3(SC\{O\}R)_2][X]$ (M = Cu or Ag; R = Me or Ph; X = PF_6, ClO_4, NO_3 or PF_6) has been isolated.[13] In the solid-state structures the

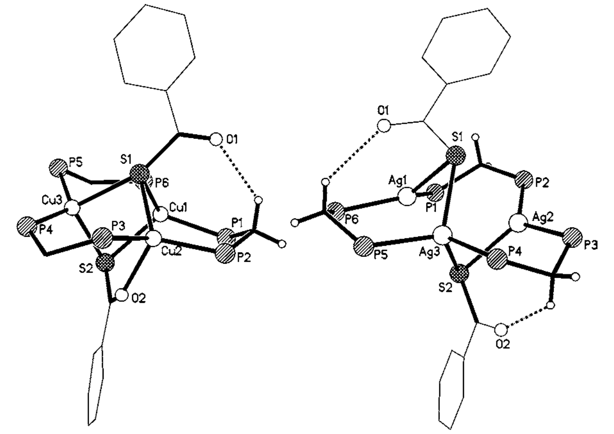


FIGURE 1. Ball and stick diagram of $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-SC}\{O\}Ph\text{-}S)(\mu_3\text{-SC}\{O\}Ph\text{-}S,O)]^{2+}$ and $[Ag_3(dppm)_3(\mu\text{-SC}\{O\}Ph\text{-}S)_2]^{2+}$ cations.

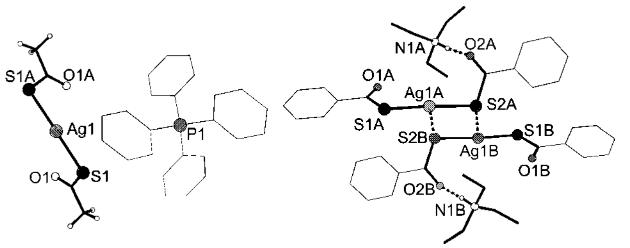


FIGURE 2. Structures of $(Ph_4P)[Ag(SC\{O\}Me)_2]$ and $[(Et_3NH)_2(Ag_2(SC\{O\}Ph)_4]$.

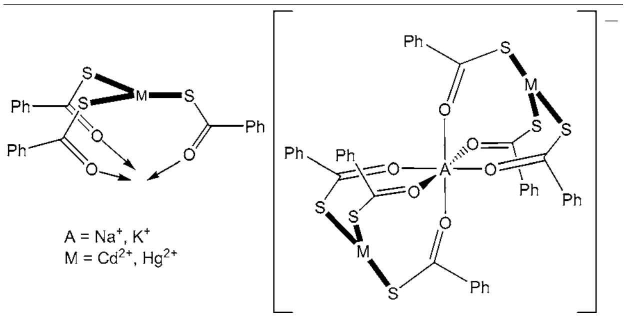
thiocarboxylate anions have μ_3-S, μ_3-S_2,O, and μ_2-S bonding modes, thereby stabilizing the trinuclear core, and C−H···O hydrogen bonding is present between one of the methylene hydrogen atoms and the carbonyl oxygen of the thiocarboxylate ligand as shown in Figure 1. ^{31}P NMR studies show that the trinuclear anions retain their solid-state structures in solution unlike the PPh_3 compounds. It is interesting to note that the ability of the capping ligand to bind to the three metals was previously thought to be responsible for the stability of the $[M_3(\mu\text{-dppm})_3]$ core since in the absence of a suitable triply bridging ligand only dimeric compounds resulted. However, our studies show that two μ_2-S bonds of thiocarboxylates are sufficient to stabilize the $Ag_3(dppm)_3$ core.

In the absence of PPh_3 homoleptic Cu(I) and Ag(I) thiocarboxylates, $(Ph_4P)[M(SC\{O\}Me)_2]$ (M = Cu or Ag) and $[(Et_3NH)_2[Ag_2(SC\{O\}Ph)_4]$ have been isolated.[14] Their anions were found to associate in the solid state, forming an ion-pair dimer when Et_3NH^+ cation was used, as shown in Figure 2.

Group 12 Metal Thio- and Selenocarboxylates

Monochalcogenocarboxylate anions, $RC\{O\}E^-$ (E = S or Se), are an interesting class of ligands due to the presence of both soft and hard bonding sites and can exhibit diverse bonding modes as discussed in the previous section. In the homoleptic transition-metal complex anions $[M(SC\{O\}Ph)_3]^-$ (M = Mn, Co, Ni, Pb) the thiobenzoate ligands are bonded to the central metal atom in a bidentate fashion.[15] On the other hand, a trigonal pyramidal geometry with a SnS_3 core has been observed in $[Sn(SC\{O\}Ph)_3]^-$ ion.[16] In contrast, Cd(II) and Hg(II) atoms in $[A\{M(SC\{O\}Ph)_3\}_2]^-$ anions (A = Na or K; M = Cd or Hg) have trigonal planar geometry with respect to the sulfur atoms.[17] In these trinuclear anions the planarity of the MS_3 core has been attributed to the presence of alkali-metal ions, which bind to the oxygen atoms of the carbonyl groups as illustrated in Scheme 3, thereby reducing their bonding to Cd(II) and Hg(II). Multi-NMR studies show concentration-dependent dissociation of the alkali-metal ions in solution.

Scheme 3. Views of the 'Claw-like' $[M(SC\{O\}Ph)_3]^-$ Ions (M = Zn, Cd, and Hg) and Its Complex with Alkali-Metal Ions



A similar trigonal planar MS_3 geometry, supported by one or more intramolecular M···O interactions, was observed in $[M(SC\{O\}Ph)_3]^-$ (M = group 12 metal ions) even when the alkali-metal ion was absent.[18] It may be noted that the trigonal planar MS_3 geometry is generally found only in complexes with hindered thiolate ligands for group 12 metal ions.[19] $(Ph_4P)[Cd(SC\{O\}Ph)_3]$ exhibits polymorphism and crystallizes in monoclinic and rhombohedral crystal systems. Of these the rhombohedral modification has a unique structure containing both planar and pyramidal CdS_3 cores.[18b] A similar planar MSe_3 kernel was also observed in the corresponding selenocarboxylates of group 12 metal ions.[20] NMR and ESI-MS studies provide evidence that complexes $[M(SeC\{O\}Tol)_n(SC\{O\}Ph)_{3-n}]^-$ (n = 0−3) persist in solution and indicate exchange between the metal selenocarboxylates and the corresponding thiocarboxylates.

The structures of the thioacetate complexes are completely different in contrast to thiobenzoates.[21a] For instance, in $[Zn(SC\{O\}Me)_3(H_2O)]^-$ anion the hydrogen atoms of the aqua ligand are hydrogen bonded to two adjacent carbonyl oxygen atoms, giving rise to approximate mirror symmetry in the tetrahedral Zn(II) complex as shown in Figure 3. Incidentally this anion represents the only synthetic structural mimic for the unusual active Zn(II) site $[(cys)_3Zn(OH_2)]$ (cys = cysteine) in 5-aminolevulinate dehydratase (ALAD).[21b] On the other hand, the CdS_3 core adapted a pyramidal geometry in the $[Cd(SC\{O\}Me)_3]^-$ anion rather than a trigonal planar geometry observed in the corresponding thiobenzoate compounds. Further, these results indicate that it is possible to isolate $[M(SC\{O\}Me)_4]^{2-}$ anionic compounds (M = Zn, Cd, and Hg), unlike those with $PhC\{O\}S^-$ ligand. Structural studies of compounds containing MS_4 tetrahedral moieties are interesting due to their relevance to bioinorganic chemistry.[22] In addition, mixed ligand complexes with chloro

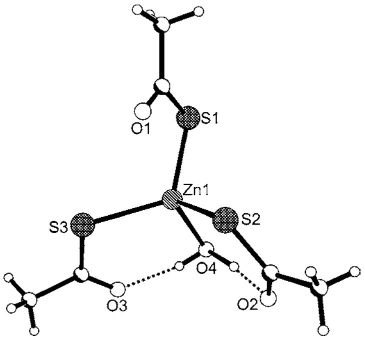


FIGURE 3. Ball and stick diagram of $[Zn(SC\{O\}Me)_3(H_2O)]^-$ as synthetic mimics of ALAD.

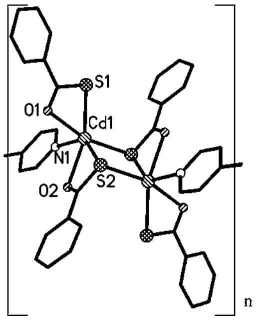


FIGURE 4. Repeating unit of the 1D polymer $[Cd_2(SC\{O\}Ph)_4(\mu\text{-bpy})]_n$.

ligands can be prepared by reacting $[M(SC\{O\}Me)_3]^-$ with Ph_4PCl. Attempts to prepare $[Cd(SC\{O\}Me)_2Cl_2]^{2-}$ resulted in formation of $(Ph_4P)_2[Cd_2(\mu\text{-Cl})_2(SC\{O\}Me)_4]$.[23a] In the salt of $[Hg_2Cl_4(SC\{O\}Ph)_2]^{2-}$ the neutral $Hg(SC\{O\}Ph)_2$ is weakly bridged by two chlorine atoms of $[HgCl_4]^{2-}$.[23b] On the other hand, in $[Hg_2Cl_2(SC\{O\}Ph)_4]^{2-}$ two $Hg(SC\{O\}Ph)_2$ moieties are bridged by two chloride ions.[23c]

Reaction between $M(SC\{O\}R)_2$ with bpy (bpy = 4,4′-bipyridine) in a 1:1 ratio gives four new 1D coordination polymers, $[\{M(SC\{O\}R)_2(\mu\text{-bpy})\}_n]$ (R = Me, Ph; M = Zn, Cd).[24] Polymer $[Cd_2(SC\{O\}Ph)_4(\mu\text{-bpy})]_n$, obtained from $Cd(SC\{O\}Ph)_2$ and bpy in a ratio of 2:1, has a unique structure in which two Cd(II) are bridged by S atoms of the two $PhC\{O\}S^-$ ligands and each oxygen atom of the bridging ligand is bonded to a Cd(II) atom, so that the two $PhC\{O\}S^-$ anions have a S_2,O bonding mode as shown in Figure 4. The bridging nature of the thiobenzoate anion observed in this coordination polymer is hitherto unknown for group 12 metal compounds.

The coordination geometry at the metal centers of the neutral $[(bipy)Cd(SC\{O\}Ph)_2]$[25a] (bipy = 2,2′-bipyridine) and $[(bipy)M(SeC\{O\}R)_2]$[25b] (M = Zn, Cd; R = Ph, CH_3-*p*-C_6H_5, Cl-*p*-C_6H_5, NO_3-*p*-C_6H_5) chelated by bipy is similar to $[M(SC\{O\}R)_2(Lut)_2]$ (M = Cd, Zn; R = CH_3, $C(CH_3)_3$; Lut = 3,5-dimethylpyridine) reported by Hampden-Smith et al.[6a]

Other Metal Thiocarboxylates

Our sustained interest in the chemistry of thiocarboxylates prompted us to explore the possibility of using the tetrahedral $[In(SC\{O\}Ph)_4]^-$ anions (M = Ga and In)[26] as metalloligands to bind to various alkali-metal ions. A new class of group 1−13 heterometallic polymers, $[A\{In(SC\{O\}Ph)_4\}(MeCN)_n]$ (A = Li, Na, K; $n = 0{-}2$) and $[A\{Ga(SC\{O\}Ph)_4\}]_n$ (A = Li, Na, K) has been synthesized.[27] The structurally characterized one-dimensional coordination polymers of In(III) consist of repeating units of alternating $[In(SC\{O\}Ph)_4]^-$ anions and alkali-metal cations as illustrated in Figure 5. Thermal decomposition of these compounds suggests formation of the corresponding ternary sulfide, AMS_2, which is a wide gap semiconductor and photocatalysis material.[28] Similarly, $[M\{In(SC\{O\}Ph)_4\}_2]$ with M = Ca and Mg have been found to be suitable single molecular precursors for MIn_2S_4 materials.[29]

Syntheses of the heterobimetallic compounds, $[(Ph_3P)CuM(SC\{O\}Ph)_4]$ (M = Ga (**8**) and In (**9**)), $[(Ph_3P)_2AgGa(SC\{O\}Ph)_4]$ (**10**), and $[(Ph_3P)_2AgIn(SC\{O\}R)_4]$ (R = Ph (**11a**) and Me (**11b**)) are illustrated in eqs 3−5.[30]

$$(Ph_3P)_2Cu(NO_3) + MX_3 + 4NaSC\{O\}Ph \rightarrow [(Ph_3P)CuM(SC\{O\}Ph)_4] \quad (3)$$

$$(Ph_3P)_2Ag(NO_3) + Ga(NO_3)_3 + 4NaSC\{O\}Ph \rightarrow [(Ph_3P)_2AgGa(SC\{O\}Ph)_4] \quad (4)$$

$$(Ph_3P)_2AgCl + InCl_3\ 4H_2O + 4NaSC\{O\}R \rightarrow [(Ph_3P)_2AgIn(SC\{O\}R)_4] \quad (5)$$

The copper(I) and silver(I) metal in complexes **8**−**11** is covalently bonded to the sulfur atom of the thiobenzoates in the metalloligand, $[M(SC\{O\}Ph)_4]^-$ as shown in Figure 6. The differences in the structural features, bonding modes of thiobenzoate ligand, number of PPh_3 bonded to Ag(I) and Cu(I), and coordination geometry at Ga(III) and In(III) have been attributed to the size and hard/soft nature of the metal ions.[30]

Single-Source Precursor for Metal Sulfides and Selenides

O'Brien et al. and Hampden-Smith et al. synthesized various metal chalcogenide thin films and nanoparticles through the single-precursor route using metal thiocarbamates and metal thiocarboxylates, respectively.[4a,b,6a,31] Inspired by their work, we focused our attention on metal sulfides and selenides. Subsequently, we collected thermogravimetric data and further characterized the products of pyrolysis of several metal thiocarboxylates and selenocarboxylates by X-ray powder diffraction (XRPD) techniques to be the corresponding metal sulfides and selenides, and the results are summarized in Table 1. Most of the precursors (except silver thiocarboxylate) give single-phase metal chalcogenides at the end of decomposition.[32] With this preliminary information we developed single-precursor routes to synthesize thin films of β-In_2S_3, $CuInS_2$, and $AgIn_5S_8$ as well as highly monodispersed colloidal nanocrystals of ZnSe,[25b] CdSe,[25b] CdS [25a] (water soluble), Ag_2Se,[12] and $Cu_{2-x}Se$.[11]

CVD is a widely used technique in depositing thin films of various semiconductor materials.[33] We found that β-In_2S_3 thin films can be obtained from **9** by MOCVD and cubic $AgIn_5S_8$ thin films can be obtained from **11a** and

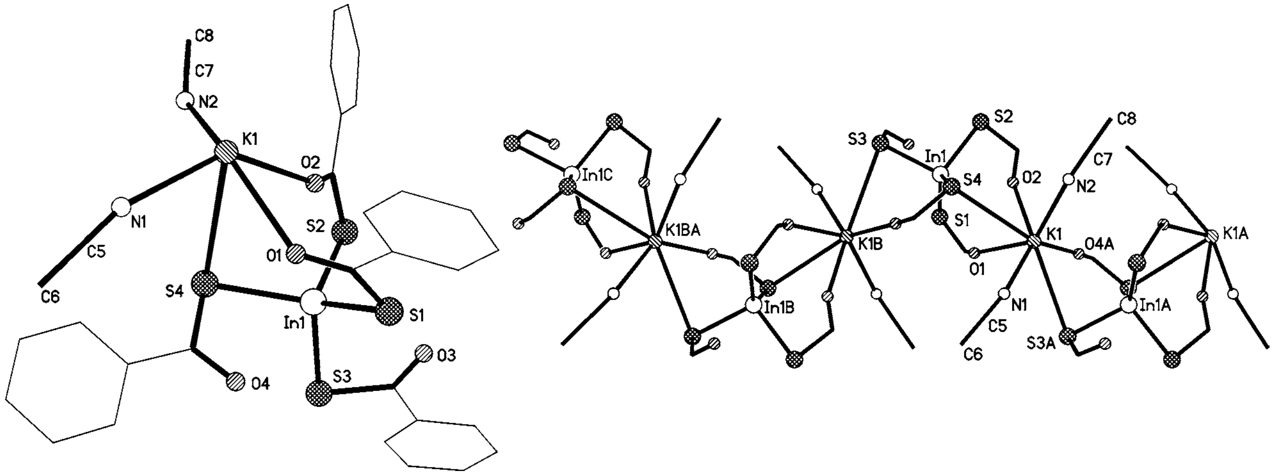
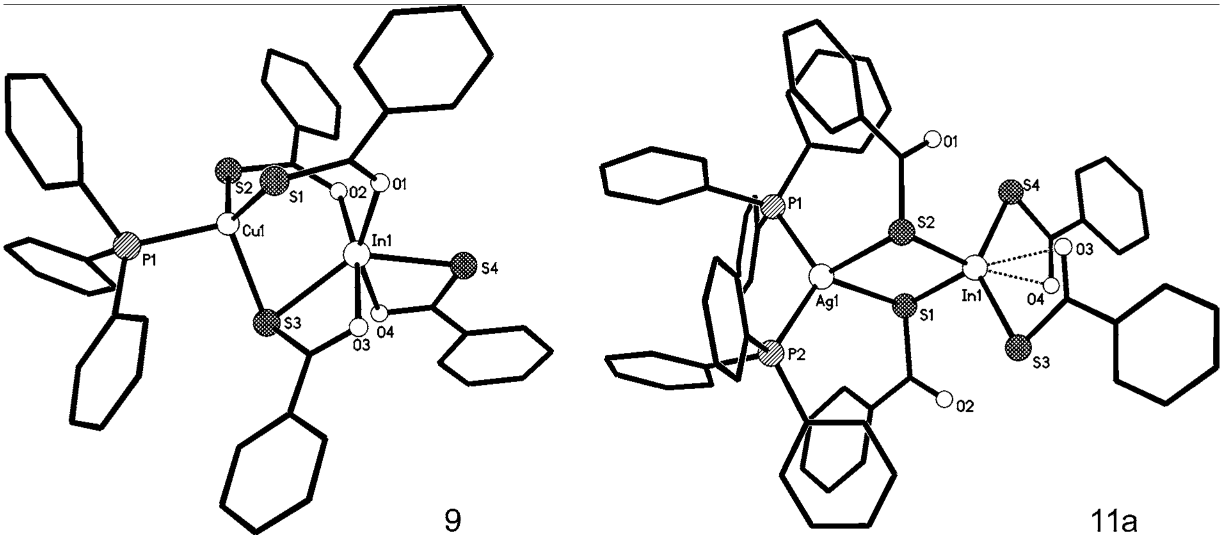


FIGURE 5. Ball and stick diagram of $[KIn(SC\{O\}Ph)_4(MeCN)_2]$ and a segment of its polymeric structure.



9

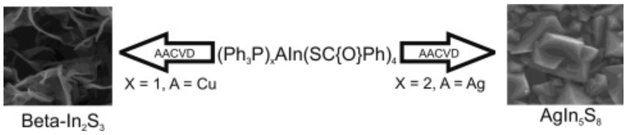
11a

FIGURE 6. Ball and stick diagrams of **9** and **11a**.

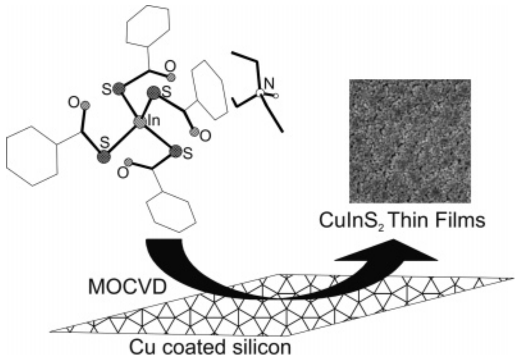
Table 1. Summary on Thermal-Decomposed Product of Metal Thiocarboxylates and Selenocarboxylates

compound	product of decomposition	ref
$[(Ph_3P)_4Cu_4(SC\{O\}Me)_4]$	orthorhombic Cu_2S	32a,c
$[(Ph_3P)_3Cu_4(SC\{O\}Ph)_4]$	tetragonal $Cu_{1.81}S$	32a,c
$[\{(Ph_3P)_2Cu\}_2(SC\{O\}Me)_2]$	hexagonal Cu_2S	32a,c
$[(Ph_3P)_2Cu(SC\{O\}Ph)]$	orthorhombic Cu_2S	32a,c
$[(Ph_3P)_2Cu(\mu\text{-}SC\{O\}Ph)_2Cu(PPh_3)]$	tetragonal and cubic $Cu_{1.96}S$	32a,c
$[(Ph_3P)_2Cu(\mu\text{-}SeC\{O\}R)_2Cu(PPh_3)]$	cubic Cu_2Se and $Cu_{2-x}Se$	11
$(Ph_4P)[M(SC\{O\}Me)_2]$ (M = Cu, Ag)	Ag_2S, Cu_2S	14
$(Et_3NH)_2[Ag_2(SC\{O\}Ph)_2]$	Ag_2S	14
silver thiocarboxylates	Ag and/or Ag_2S	32a,c
$[(Ph_3P)_2Ag(\mu\text{-}SeC\{O\}R)_2Ag(PPh_3)]$	orthorhombic Ag_2Se	12
$[\{Zn(SC\{O\}R)_2(\mu\text{-bpy})\}_n]$ (R = Me, Ph)	cubic ZnS	24
$[\{Cd(SC\{O\}Me)_2(\mu\text{-bpy})\}_n]$	cubic CdS	24
$[\{Cd(SC\{O\}Ph)_2(\mu\text{-bpy})\}_n]$	hexagonal CdS	24
$[(2,2'\text{-bipyridine})Cd(SC\{O\}Ph)_2]$	cubic CdS	25a
$[(2,2'\text{-bipyridine})Zn(SeC\{O\}Ph)_2]$	cubic ZnSe	25b
$[(2,2'\text{-bipyridine})Cd(SeC\{O\}Ph)_2]$	hexagonal CdSe	25b
$[RNH][In(SC\{O\}R)_4](H_2O)_n$ (R = Et, n-Bu; R = Me, Ph; $n = 0, 1$)	tetragonal In_2S_3	32b
$[Et_3NH][Ga(SC\{O\}Ph)_4](H_2O)$	monoclinic Ga_2S_3	32b
$[(Ph_3P)_2AgIn(SC\{O\}R)_4]$ (R = Me, Ph)	orthorhombic $AgInS_2$	30
$[(Ph_3P)CuIn(SC\{O\}Ph)_4]$	tetragonal $CuInS_2$	30
$[(Ph_3P)CuGa(SC\{O\}Ph)_4]$	tetragonal $CuGaS_2$	30
$[(Ph_3P)_2AgGa(SC\{O\}R)_4]$	tetragonal $AgGaS_2$	30
$[A\{M(SC\{O\}Ph)_4\}(MeCN)_n]$ (A = Li, Na, K; M = In, Ga; $n = 0{-}2$)	AMS_2 (A = Li, Na, K; M = Ga, In) bulk materials	27
$[M\{In(SC\{O\}Ph)_4\}_2]$ (M = Ca, Mg)	MIn_2S_4 (M = Ca, Mg)	29

Scheme 4. Diagram Illustrating the Deposition of β-In_2S_3 and $AgIn_5S_8$ Thin Films from 11a and 11b by AACVD



Scheme 5. Diagram Illustrating the Thin Film Deposition of $CuInS_2$ from $(Et_3NH)[In(SC\{O\}Ph)_4]\cdot H_2O$

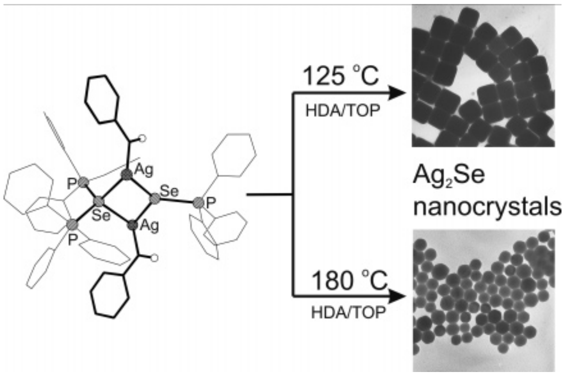


11b by AACVD techniques, as shown in Scheme 4.[30] Further, **11a** and **11b** are the first single molecular precursors used to deposit $AgIn_5S_8$ thin films, the morphology of which is found to be sensitive to the growth temperature. To our surprise, the expected thin films of $CuInS_2$ and $AgInS_2$ were not deposited by AACVD techniques, although pyrolysis experiments indicated formation of these powders. The ESI-MS study showed no molecular ion peak of **9**; however, signals due to $[In(SC\{O\}Ph)_4]^-$, $[(PPh_3)_2Cu]^+$, and $[(PPh_3)_3Cu]^+$ molecular ions were identified. This suggested dissociation of the precursor in solution during the AACVD process.

An elegant method to deposit high-quality $CuInS_2$ thin films from MOCVD was accidentally discovered by employing a copper-coated silicon substrate and $(Et_3NH)[In(SC\{O\}Ph)_4].H_2O$.[32b,34] It is likely that reaction between the precursor and/or the decomposed product $(PhCO)_2S$ and the copper substrate resulted in formation of Cu_2S,[6a] while In_2S_3 is deposited on the surface of the substrate. Solid-state reaction between the copper sulfide and indium sulfide then resulted in formation of $CuInS_2$ thin films. When the substrate was replaced by nickel-coated silicon, only the In_2S_3 thin film formed (Scheme 5). Attempts to grow Ga_2S_3 and $CuGaS_2$ thin films in a similar way yielded thin films containing a mixture of metal sulfides. It appears that the $CuGaS_2$ decomposition temperature is much lower than the temperature required, producing metal thiocarboxylate precursor vapors.[32b]

Controlling the monodispersity, size, and shape of the nanoparticles, which are important to manipulate the quantum-confined properties, still remains a challenge in colloidal synthesis.[4b] We have shown that the orthorhombic Ag_2Se nanocrystals can be prepared by thermally decomposing $[(Ph_3P)_2Ag(\mu\text{-}SeC\{O\}Ph)_2Ag(PPh_3)]$ in the presence of hexadecylamine (HDA) and tri-*n*-octylphosphine (TOP) in the temperature range 125−180 °C under anaerobic conditions. Further, the morphology of such nanocrystals can be tuned from cubic-shaped to faceted crystals as shown in Scheme 6.[12] Both the temperature and the concentration of the amine are the two major factors influencing the morphology of these Ag_2Se nanocrystals. It is clearly visible from the TEM images that the unique shape of the Ag_2Se nanocrystals and uniform size induce self-assembly of these nanoparticles, which are essential for photonic studies. In addition, the Ag_2Se cubes undergo a smooth and reversible phase transition from the orthorhombic to the cubic phase on heating, just like the bulk material, without affecting the crystallinity.

Scheme 6. Formation of Ag_2Se Nanocrystals of Different Shapes Under Different Experimental Conditions



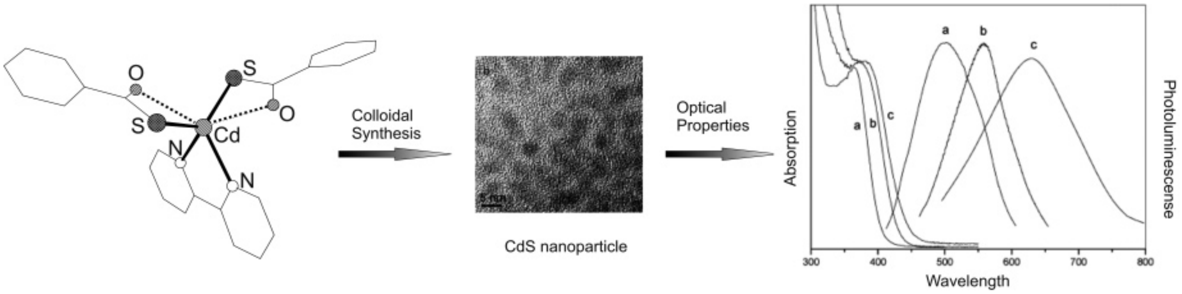
A similar copper selenocarboxylate precursor $[(Ph_3P)_2Cu(\mu\text{-}SeC\{O\}Ph)_2Cu(PPh_3)]$ has also been used to synthesize nonstoichiometric monodispersed $Cu_{2-x}Se$ nanoparticles in a mixture of tri-*n*-octylphosphine oxide (TOPO) and TOP solution at elevated temperature.[11] Unlike Ag_2Se, these $Cu_{2-x}Se$ nanoparticles are spherical in shape and the morphology of the nanocrystals is less dependent on the reaction conditions.

Chin et al. have shown that cubic-shaped or faceted Ag_2S nanocrystals can be synthesized by thermally decomposing $[Ag(SC\{O\}Ph)]$ in a mixture of TOP and HDA at 80−120 °C.[7] It is likely that mixing $[Ag(SC\{O\}Ph)]$ with excess TOP will lead to formation of $[(TOP)_2Ag(SC\{O\}Ph)]$.[8] Interestingly, although a similar synthesis was used to prepare both Ag_2S and Ag_2Se nanoparticles, different growth mechanisms were proposed for these two nanocrystals.[7,12]

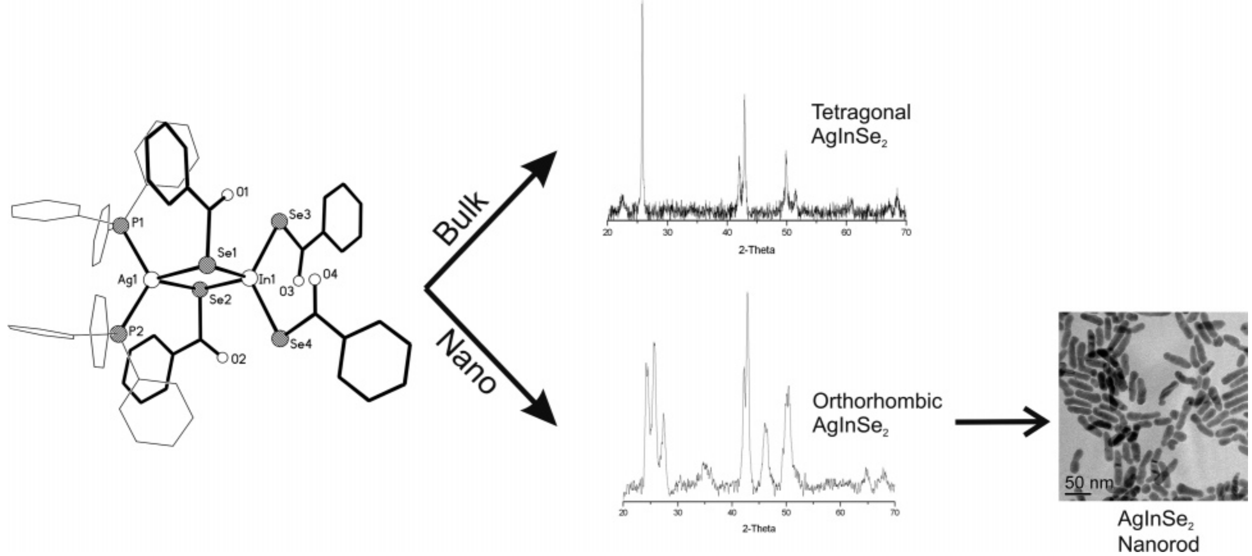
Recently, PbS nanocrystals were obtained from amine-induced decomposition of $[Pb(SC\{O\}Ph)_2]$ at room temperature.[35] It is found that amine acts as both the catalyst and the capping agent in the synthesis. When ethylenediamine was used, PbS dendrites were obtained exclusively. Further, morphology tuning of the dendrites to induce 1D growth into nanorods is achievable through addition of a trace amount of dodecanethiol.

The unique physicochemical and optical properties of group 12 metal chalcogenide semiconductor nanocrystals have attracted much research interest over the years.[36] We found that ZnSe and CdSe quantum dots in the size range 4−10 nm can be prepared in a one-pot reaction from thermal decomposition of the corresponding metal selenocarboxylate in the TOPO/TOP solution at elevated temperature.[25b] During synthesis the size and shape of the nanocrystals were not found to depend on reaction

Scheme 7. Water-Soluble Luminescent CdS Nanocrystals from [(bipy)Cd(SC{O}Ph)$_2$]



Scheme 8. Diagram Illustrating the Formation of AgInSe$_2$ Bulk and Nanoparticles from [(Ph$_3$P)$_2$AgIn(SeC{O}Ph)$_4$]



conditions very much, and hence, this method may be suitable for scaling up. Water-soluble nanoparticles are useful in bioimaging applications. Recently, it was shown that the water-soluble CdS nanoparticles can be prepared by refluxing the [(bipy)Cd(SC{O}Ph)$_2$] precursor in the presence of 1-thioglycerol in basic aqueous solution.[25a] These CdS quantum dots in the size range 25−40 Å have been obtained by varying the capping agent-to-precursor molar ratio. Moreover, the prepared CdS nanocrystals (as shown in Scheme 7) exhibit quantum confinement effect, and an interesting dimerization of CdS nanoparticles was observed. Particle aging kinetics was found to follow the Ostwald ripening mechanism.[37]

Optical and photovoltaic properties of I-III-VI-type chalcopyrite materials have been actively investigated for possible applications in solar cell technologies,[38] and hence, efforts have been made to obtain the bulk and thin films of the corresponding materials by newer synthetic methods.[30,39] In contrast, few groups have reported the syntheses of I-III-VI-type chalcopyrite nanoparticles.[40] Our recent studies have shown that high-quality monodispersed AgInSe$_2$ nanorods can be synthesized by thermal decomposition of [(PPh$_3$)$_2$AgIn(SeC{O}Ph)$_4$] in hot oleylamine and dodecanethiol, and the synthesized AgInSe$_2$ nanorods are isostructural to the corresponding sulfide (Scheme 8).[41] This metastable orthorhombic phase AgInSe$_2$ which has not been reported so far is stabilized by the capping agents. Such monodispersed colloidal ternary chalcogenide nanocrystals are rare. On the other hand, toluene-soluble high-temperature orthorhombic AgInS$_2$ nanocrystals obtained by decomposing **14a** in dodecanethiol and oleic acid at 125−200 °C show significant third-order NLO properties.[42]

Conclusion

We developed synthetic routes to a wide variety of thermally stable metal thiocarboxylates and selenocarboxylates. The chemistry of these metal−monochalcogenocarboxylates is not always similar, as observed between the thiolates and selenolates.[43] They exhibit interesting yet diversified structural motifs with variable bonding modes. The anions, viz., [M(SC{O}Ph)$_3$]$^-$ and M(SC{O}Ph)$_4$]$^{2-}$, have been used as metalloligands to bind to alkali-metal ions. Many of these metal complexes have been used as single molecular precursors to metal sulfide and selenide powders, thin films, and nanocrystals. Low-temperature synthesis of a number of ternary sulfides and selenides, AME$_2$ (A = Li, Na, K; M = Ga, In; E = S, Se) has opened the door to materials scientists to explore their solid-state properties. Use of some of these metal thiocarboxylates to make thin films of ternary metal sulfides has also been demonstrated. It is possible to synthesize the precursors suitable for making nanocrystals of metal sulfides and selenides by design. This work, which started off as an academic curiosity, is now leaping toward the area of inorganic materials. The glaring omission of the chemistry of metal tellurocarboxylates in this Account will fuel our interest in that direction in the future.

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