Inorganic Chemistry © Cite This: Inorg. Chem. XXXX, XXX, XXX, XXX-XXX

Aerosol-Assisted Chemical Vapor Deposition of ZnS from Thioureide **Single Source Precursors**

Hannah S. I. Sullivan,[†] James D. Parish,[†] Prem Thongchai,[†] Gabriele Kociok-Köhn,[‡] Michael S. Hill,[†] and Andrew L. Johnson*,[†]®

[†]Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

*Materials and Chemical Characterisation Facility (MC2), Department of Chemistry, University of Bath. Claverton Down, Bath, BA2 7AY, U.K.

S Supporting Information



ABSTRACT: A family of 12 zinc(II) thoureide complexes, of the general form $[{L}ZnMe], [{L}Zn{N(SiMe_3)_2}], and$ $[{L}_2Zn]$, have been synthesized by direct reaction of the thiourea pro-ligands $PrN(H)CS(NMe_2)$ H[L¹], CyN(H)CS(NMe_2) $H[L^3]$, $^tBuN(H)CS(NMe_2)$ $H[L^2]$, and $MesN(H)CS(NMe_2)$ $H[L^4]$ with either $ZnMe_2$ (1:1) or $Zn\{N(SiMe_3)_2\}_2$ (1:1 and 2:1) and characterized by elemental analysis, NMR spectroscopy, and thermogravimetric analysis (TGA). The molecular structures of complexes $[{L^1}ZnMe]_2(1), [{L^2}ZnMe]_2](2), [{L^3}ZnMe]_{\infty}(3), [{L^4}ZnMe]_2](4), [{L^1}Zn{N(SiMe_3)_2}]_2$ (5), $[\{L^2\}Zn\{N(SiMe_3)_2\}]_2$ (6), $[\{L^3\}Zn\{N(SiMe_3)_2\}]_2$ (7), $[\{L^4\}Zn\{N(SiMe_3)_2\}]_2$ (8), $[\{L^1\}_2Zn]_2$ (9), and $[\{L^4\}_2Zn]_2$ (12) have been unambiguously determined using single crystal X-ray diffraction studies. Thermogravimetric analysis has been used to assess the viability of complexes 1-12 as single source precursors for the formation of ZnS. On the basis of TGA data compound 9 was investigated for its utility as a single source precursor to deposit ZnS films on silica-coated glass and crystalline silicon substrates at 150, 200, 250, and 300 °C using an aerosol assisted chemical vapor deposition (AACVD) method. The resultant films were confirmed to be hexagonal-ZnS by Raman spectroscopy and PXRD, and the surface morphologies were examined by SEM and AFM analysis. Thin films deposited from (9) at 250 and 300 °C were found to be comprised of more densely packed and more highly crystalline ZnS than films deposited at lower temperatures. The electronic properties of the ZnS thin films were deduced by UV–Vis spectroscopy to be very similar and displayed absorption behavior and band gap (E_{φ} = 3.711-3.772 eV) values between those expected for bulk cubic-ZnS (E_g = 3.54 eV) and hexagonal-ZnS (E_g = 3.91 eV).

INTRODUCTION

As one of the first semiconducting materials to be discovered, zinc sulfide (ZnS) is the prototype II-VI semiconductor and has habitually displayed remarkable fundamental properties and versatility of application, finding utility in a wide range of areas such as electronics and optoelectronics, photovoltaic cells, optical sensors, lasers, infrared windows, electroluminescent and photoluminescent devices, antireflection coatings, reflectors, interference filters, and displays.

Understanding the relationship between structural and electronic properties of semiconducting materials is crucial to the design of novel nanostructures with tunable properties. Zinc sulfide exists in three polymorphic forms:² cubic zinc blende (ZB-ZnS, also called β -ZnS or "sphalerite"), hexagonal Wurtzite (W-ZnS), or the rarely observed cubic rock salt (RS- ZnS),³ with each phase possessing unique physical properties.⁴ In both cubic and hexagonal structures, Zn and S atoms exist in tetrahedral environments, where the only difference is in the stacking sequence of atomic layers. A consequence of this difference in the physical arrangement of the atoms within the lattice is the difference in band gap energy observed for ZB-ZnS ($E_g = 3.54 \text{ eV}$) and W-ZnS ($E_g = 3.91 \text{ eV}$).²

Zinc sulfide is generally considered one of the best materials available as a buffer layer for the fabrication of CIGS solar cells. ZnS provides a nontoxic and environmentally safe alternative to cadmium sulfide and displays improved lattice matching to CIGS absorbers in addition to being capable of transmitting

Received: December 5, 2018

higher energy photons and increasing light absorption in the absorber layer (cf. CdS).⁵

A wide range of thin film deposition techniques⁶ have been applied to the fabrication of ZnS thin films. From a commercial and technological viewpoint, many of these techniques entail high operating cost and often require complicated operational steps and instrumentation, without the guarantee of high reproducibility. As such, studies have focused on routes by which high quality ZnS thin films can be produced at low cost in a consistent and reproducible manner.

To this end, a variety of metalorganic complexes of zinc (including dialkyldithiocarbamates,^{1d,7} alkyl xanthates,⁸ thiosemicarbazones,⁹ dialkylthiocarbamates and monothiocarboxylates,¹⁰ dithiophosphinate,¹¹ N-thiophosphorylated-thioureas,¹² and thio- and dithio-biuret¹³) have been designed and developed for application in the chemical vapor deposition (CVD) of ZnS thin films.¹⁴ Reviews by Gleizes¹⁵ and O'Brien^{14b,16} provide detailed accounts of the use of other single source precursors for the deposition of chalcogenide materials by MOCVD. Of these precursors, $[Zn(S_2CNEt_2)_2]$ was the first precursor compound employed, yielding only poor quality ZnS via a low-pressure CVD (LP-CVD) process. Reports suggest that the implementation of $[Zn(S_2CNEt_2)_2]$ in other thin film deposition methods can produce good quality hexagonal and cubic ZnS films on Si(111) substrates,¹⁷ and in related studies, nanocrystalline W-ZnS thin films have been deposited on crystalline silicon and silicon dioxide substrates by CVD from $[Zn(S_2COR_2)_2]$ (R = Et or ⁱPr).^{8a,}

Many of these systems, however, suffer from inconveniently low precursor volatility unless used at very low pressures.^{14b,15,18} An alternative variant on the CVD technique, which circumvents this limitation and avoids the use of highly reactive metal alkyls or H2S, is aerosol-assisted CVD (AACVD),¹⁹ where the only restriction on precursor identity in this respect is its solubility in appropriate solvents, with the subsequent solutions nebulized and transported as micron-scale droplets to a heated substrate.^{18,20} Despite its obvious advantages, however, only the monothiocarboxylate complexes $[Zn(SOCMe)_2(tmeda)]$ and $[Zn(SOC^tBu)_2(tmeda)]$ (tmeda) = $N_1N_2N_2N_3N_3$ the tetramethylethylenediamine) and the tetramethyldithiobiurete complex $[Zn{(SC(NMe_2))_2N}_2]$ have been utilized in AACVD studies to date. The former of these two complexes produced thin films in which mixtures of ZB-ZnS and W-ZnS were observed at temperatures as low as 125 °C,^{10a} while the latter deposited ZB-ZnS below 350 °C and W-ZnS at deposition temperatures above 400 °C.^{13a,14b}

Recently we described the design and synthesis of metal precursors based around thioamidate²¹ and thioureide²² ligand systems for the production of metal sulfide thin films by AACVD processes. In the present work, we describe the synthesis and characterization of a family of 12 homo- and heteroleptic zinc-thioureide complexes, which have been synthesized by direct reaction of the free thioureates with either ZnMe₂ (1:1) or Zn{N(SiMe₃)₂} (1:1 and 2:1). We also report the potential of selected complexes to act as single source precursors to thin films of ZnS.

RESULTS AND DISCUSSION

Synthesis. The thiourea pro-ligands, HL^1-HL^4 , were prepared by direct reaction of the appropriate commercially available isothiocyanates with anhydrous $HNMe_2$ in hexane (Scheme 1), followed by isolation by filtration, washing with fresh hexane, and drying in-vacuo to yield the pure pro-ligands



as colorless microcrystalline powders in high yields (81-86%). In all cases, the products were characterized by solution state NMR (¹H and ¹³C) spectroscopy and elemental analysis.

The ¹H NMR spectra of the pro-ligands all display a resonance ca. δ 4.42–5.64 ppm associated with the {NMe₂} functionality, a feature which is absent from the starting thioisocyanates, while the ¹³C{¹H} NMR spectra demonstrate a characteristic shift in the resonance associated with the thioisocyanates' {S=C=N} carbon resonance from δ 129–134 ppm to δ 182–183 ppm for the {C=S} double bonds.

The zinc thioureide derivatives, compounds 1-4 and 5-8, were readily synthesized through the reaction in hexane of 1 equivalent of either $[ZnMe_2]$ or $[Zn\{N(SiMe_3)_2\}_2]$ with the pro-ligands HL^1 , HL^2 , HL^3 , and HL^4 and were isolated as colorless solids (Scheme 2).

The reaction of both $[ZnMe_2]$ and $[Zn\{N(SiMe_3)_2\}_2]$ with the pro-ligands HL^1 - HL^4 in a stoichiometric 1:1 reaction results in the formation, and isolation after recrystallization, of the monothioureide complexes 1-4 and 5-8, respectively. The ¹H NMR spectra clearly show the absence of the broad singlet resonance associated with the {NH} group in the proligands, indicating loss of this acidic proton as either CH₄ or $HN(SiMe_3)_2$. In the case of complexes 1, 2 and 4, and 5-8, the complexes are all soluble in C₆D₆ whereas in contrast, complex 3 displayed limited solubility in C₆D₆, suggestive of subtle differences between the solution state structures of complexes 3 and 7. Despite this observation, the ¹H NMR spectra of the respective compounds clearly show the presence of singlet resonances at $\delta = -0.01$ ppm (1), 0.05 ppm (2), 0.01 ppm (3), and 0.41 ppm (4), representative of the {Zn-Me} moiety in compounds 1–4, and at $\delta = 0.46$ ppm (5), 0.46 ppm (6), 0.44 ppm (7), and 0.31 ppm (8) in compounds 5-8, representative of a $\{Zn-N(SiMe_3)_2\}$ moiety. These resonances appear in relative ratios of 3H:6H and 18H:6H respectively, with the dimethylamine group, $\{NMe_2\}$, of the ligands $\{L^1\}$ - $\{L^4\}$, indicative of the presence of the thioureide ligand and $\{Me\}$ or $\{N(SiMe_3)_2\}$ groups in a 1:1 ratio as expected for the formation of the heteroleptic methyl-zinc thiouride complexes 1-4 and the amide zinc thiouride complexes 5-8 (Scheme 2). Elemental analyses of the products are consistent with the formation of the heteroleptic complexes [{L}ZnMe], 1–4, and $[{L}Zn-N(SiMe_3)_2]$, 5–8, respectively.

Comparable reaction of the pro-ligands $HL^{1}-HL^{4}$ with $[Zn{N(SiMe_{3})_{2}}]$ in a 2:1 ratio results in the formation of the *bis*-thioureide complexes, **9–12**, in moderate to high isolated yields (56–83%). In contrast to the ¹H NMR spectra of **5–8**, the ¹H NMR spectra of **9–12** clearly show the absence of resonances associated with the {N(SiMe_{3})_{2}} units (ca. 0.31– 0.48 ppm) and are consistent with the formation of the *bis*-thioureide complexes (Scheme 3). The appearance of only one set of resonances in the ¹H and ¹³C NMR spectra for the thioureide ligands in all four sets of spectra is indicative of the fact that the ligands occupy identical environments on the

Scheme 2



Scheme 3



NMR time scale. Elemental analysis of 9-12 is consistent with the formation of the *bis*-thioureide complexes.

Solid State Molecular Structures. X-ray quality single crystals of compounds 1-4, 5-8, 9, and 12 were obtained from a saturated toluene solution at -28 °C. Figure 1 shows the molecular structure of compounds 1, 2, and 4, which present as an essentially iso-reticular series consisting of dimeric molecular units, $[{L}ZnMe]_2$.



Figure 1. Molecular structure of $[{L^1}ZnMe]_2$ (1). Thermal ellipsoids are shown at 50% probability. Symmetry transformations used to generate equivalent atoms: -X + 1, -Y, -Z + 1.

Complex 1, which crystallizes in the monoclinic space group $P2_1/n$, forms a centrosymmetric dimer with anti-arrangement of the thioureide ligands about the central $\{Zn_2S_2\}$ metallocycle, similar to the amidinate and dithiocarbamate systems $[\{{}^{t}BuC(Ni-Pr)_2\}ZnMe]_2^{23}$ and $[\{Et_2NCS_2\}ZnMe]_2^{.7b}$ Each thioureide ligand can be best described as being coordinated to the zinc centers in a $\mu_i \kappa^2 : \kappa^1$ coordination mode, i.e. η^2 -N₃S-

Article

chelating fashion to one zinc center, while participating in a Sbridging interaction with an adjacent zinc center. While each zinc atom in the series of complexes is four coordinate, the coordination at the metal is not simply described in terms of any regular polyhedron. In the case of complex 1, the geometry about the zinc atoms is best described as distorted trigonal pyramidal, with the base defined by the atoms C(3), N1(12)and $S(1)^* [\sum_{Z_n} = 354.54(6)^\circ]$. Coordination of the sulfur atom from the chelating thioureide, Zn-S_{int} [2.5348(7) Å], which is significantly longer than the dimer-forming exocyclic $Zn-S^*_{exo}$ interaction [2.4474(7) Å], completes the coordination environment and distorts the geometry away from ideal due to the restricted S(1)-Zn(1)-N(11) bite angle [68.10°]. The Zn-Me bond [1.970(3) Å] is similar to those found in related complexes.^{7b} The C–S bond length [1.775(3) Å] is close in value to that expected for typical C-S single bonds, whereas the C-N bond [1.362(3) Å] is more consistent with its assignment as a localized C=N double bond. Despite the approximate coplanarity of the $\{CNS\}$ and $\{NMe_2\}$ moieties (the angle between the two planes is $\sim 27.79^{\circ}$) within the thioureide ligand, there is no evidence of multiple bonding character between {CNS} and {NMe₂} groups, as indicated by the approximately single C–N bond [1.301(3)Å]. The same general trends observed in complex 1 are repeated in complexes 2 and 4. Table 1 shows selected bond lengths and angles for complexes 1, 2, and 4, and their molecular structures are shown in Figure 2.

In stark contrast to the molecular structures of complexes 1, 2, and 4, the solid state structure of 3, containing the sterically more demanding ^tBu group, adopts a rather unexpected structure in the solid state, favoring the formation of a polymeric system in which the coordination mode of the thioureide moiety differs significantly from that observed in 1, 2, and 4. The molecular structure of complex 3 is shown in Figure 3 and selected bond lengths and angles in Table 2.

Complex 3 crystallizes in the orthorhombic space group $P2_12_12_1$ with one complete molecule in the asymmetric unit cell. The asymmetric units are connected in the form of one-dimensional zigzag polymeric chains extended along the crystallographic *a*-axis. As with complexes 1, 2, and 4 the zinc metal center possesses a 4-coordinate geometry. Unlike 1, 2, and 4, however, the coordination environment is made up of the two nitrogen atoms of the thioureide ligand, the carbon of the terminal {Me} group and the {S} atom of an adjacent [{L³}ZnMe] unit. This contrasting κ^2 -*N*,*N'* coordination mode of the thioureide ligand is comparable to that observed in the related ureide-coordinated complex [Sn{ κ^2 -*N*,*O*-OC(NMe₂)-N^tBu}{ κ^2 -*N*,*N'*-N(^tBu)C(S)NMe₂}].²⁴ The coordination

	1	2	4
Zn-Me	1.970(3) Å	1.963(2) Å & 1.968(2) Å	1.965(4) Å
Zn-S _{int}	2.5348(7) Å	2.5295(6) Å & 2.5374(6) Å	2.5217(10) Å
Zn-N	2.036(2) Å	2.0261(16) Å &2.0253(16) Å	2.046(3) Å
Zn-S _{exo}	2.4474(7) Å	2.4447(5) Å & 2.4493(5) Å	2.4748(10) Å
C–NMe ₂	1.362(3) Å	1.354(3) Å & 1.354(3) Å	1.350(4) Å
S-C	1.775(3) Å	1.7821(19) Å & 1.7834(19) Å	1.788(3) Å
N-C	1.301(3) Å	1.308(3) Å & 1.308(3) Å	1.307(4) Å
S–Zn–N	68.10(5)°	68.20(5)° & 67.85(5)°	$68.20(8)^{\circ}$



Figure 2. Molecular structure of A: $[{L^3}ZnMe]_2$ (2) and B: $[{L^4}ZnMe]_2$ (4). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms in B: -X + 1, -Y + 1, -Z.



Figure 3. A projection along the *c* axis showing both the molecular structure of $[\{L^3\}ZnMe]_{\infty}$ (3) and the formation of the one-dimensional polymeric chains. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms in 3: * -X + 1, Y + 1/2, -Z + 3/2; ** -X + 1, Y - 1/2, -Z + 3/2.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 3 $\,$

	3
Zn-Me	1.968(3) Å
Zn-N ^t Bu	2.090(2) Å
Zn←NMe ₂	2.203(2) Å
Zn····S	2.3540(8) Å
C-NMe ₂	1.472(4) Å
S-C	1.743(2) Å
^t BuN-C	1.268(3) Å
^t BuN–Zn–NMe ₂	62.57(9)°
Me-Zn…S	$124.54(10)^{\circ}$

mode of the thioureide ligand in **2** can be best described as being *N*,*N'*-chelating (κ^2) to the zinc atom along with the terminal {C=S} acting as a bridging atom to an adjacent zinc center. The central planar carbon atom of the thioureide ligand is appended by a sulfur atom, with a S–C bond length indicative of significant double character (1.743 Å), in addition to the {N^tBu} and {NMe₂} moieties. The carbon–nitrogen bonds at 1.268(3) Å and 1.472(4) Å, respectively, are approaching values observed for {C=N^tBu}²⁵ and {C-NMe₂}^{25b} bonds, indicative of some delocalization of charge across the {S–C–N^tBu} moiety.

The bond angles around the zinc atom in 3 are in the range expected for a more tetrahedral geometry cf. 1, 2, and 4. The

Zn–C bond lengths observed in 3 (1.968(3) Å) are comparable to those described above and are in the typical range reported for Zn-Me groups.^{7b} The Zn–N^tBu (Zn–N = 2.090(2) Å)^{25b} and Zn \leftarrow {NMe₂} bond lengths (Zn–N = 2.203(3) Å)²⁶ are also in the range expected for comparable bonds in literature complexes. The intermolecular Zn…S bond (2.3540(8) Å) is comparable to that found in zinc blende (~2.342 Å).^{1c}

In the case of the *bis*-trimethylsilyl derivatives **5**–**8**, there is no comparable change in the coordination mode of the thioureide ligand as the series traverses from ⁱPr to Cy, ^tBu, and Mes ligand systems. In general, the solid state molecular structures of **5**–**8** possess a comparable structural topology with the κ^2 -N,S complexes **1**, **2**, and **4**, with the {N(SiMe₃)₂} group taking the terminal position adopted by the methyl groups. Figure 4 shows the molecular structure of **7**. Selected



Figure 4. Molecular structure of $[{L^3}Zn{N(SiMe_3)_2}]_2$ (7). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: -X, -Y, -Z + 1.

bond lengths and angles for complexes 5-8 are shown in Table 3. The molecular structures of 5, 6, and 8 are shown in the Supporting Information.

Compound 7 crystallizes in the triclinic space group $P\overline{1}$ with two independent halves of the dimeric compound $[{L^3}Zn{N(SiMe_3)_2}]_2$ in the asymmetric unit cell. Complexes 5, 6, and 8 also crystallize in the triclinic space group $P\overline{1}$, with onehalf of the respective dimer unit present in the asymmetric unit cells for complexes 5 and 8, and two independent halves of the dimeric unit in 6. As with complexes 1, 2, and 4, the thioureide ligands in 5–8 are coordinated to the zinc centers in a $\mu, \eta^2: \eta^1$ - coordination mode and, as with the methyl-zinc complexes described earlier, the molecular structures of **5**–**8** exist as centrosymmetric dimers with an anti-arrangement of ligands about the central $\{Zn_2S_2\}$ metallocycle. The molecular structure of complex 7 is described here as an exemplar with similar features to those observed in complexes **5**, **6**, and **8**.

The {Zn₂S₂} core of 7 is planar and forms an angle of 77.0° to the equally planar {ZnNCS} metallocycle. As with complex 1, the geometry about zinc atoms in complexes **5–8** is best described as distorted trigonal pyramidal, with the base defined by the atoms N(2), N(11), and S(1)* [$\sum_{Zn} = 354.11(6)^{\circ}$] (5: $\sum_{Zn} = 355.88(5)^{\circ}$, 6: $\sum_{Zn} = 355.55(11)^{\circ}$, 8: $\sum_{Zn} = 347.58(4)^{\circ}$). As in 1, 2, and 4, a strong interaction between the two "'monomeric'" [{L³}Zn{N(SiMe₃)₂}] units is indicated by the shorter Zn–S distance [2.0831(19) Å] compared with Zn–S [2.1879(18) Å].

Coordination of the sulfur atom from the chelating thioureide, $Zn-S_{int}$ [2.5171(6) Å], which is significantly longer than the dimer forming exocyclic $Zn-S^*_{exo}$ interaction [2.3837(6) Å], completes the coordination environment and distorts the geometry away from ideal due to the restricted S(1)-Zn(1)-N(11) bite angle [68.55(5)°].

The remaining Zn–N bond of the chelating {L³} anion is marginally longer [2.0746(18) Å] than the analogous bonds in compounds 1, 2, and 4. The Zn–N amide distance [1.9141(18) Å] is comparable to the structurally related [{hpp}Zn{N(SiMe₃)₂}]₂ ({hpp} = 1,3,4,6,7,8-hexahydro-2Hpyrimido[1,2-*a*]pyrimide) in which the zinc geometry is described as distorted tetrahedral.²⁷

Single crystals of the *bis*-thioureide complexes 9 and 12 were obtained independently from solutions of toluene upon storage at -28 °C. Complexes 9 and 12 crystallize in the monoclinic space group I2/a and the triclinic space group $P\overline{1}$, respectively. For 9 the asymmetric unit cell contains one $[{L^1}_2Zn]$ molecule, alongside one molecule of toluene, with symmetry operators generating the second half of the dimeric $[{L^1}_2Zn]_2$ system (Figure 5). Similarly for 12 the asymmetric unit cell contains one complete $[{L^4}_2Zn]$ molecule, with symmetry operators generating the second half of the dimeric $[{L^4}_2Zn]_2$ system (Figure 5). Table 4 shows selected bond lengths and angles for complexes 9 and 12

The molecular structures of 9 and 12 are related to those of complexes 1, 2 and 4, and 5-8, which have been previously described, and are based on dimeric molecules with highly distorted five-coordinate geometries about each zinc atom, comprising the sulfur and nitrogen atoms of the two chelating thioureide ligands. The fifth, and final, coordinating atom is found to be a sulfur atom belonging to an adjacent chelating thioureide ligand, bridging two zinc atoms and resulting in the formation of three fused four membered rings, i.e. {ZnSCN}/

Table 3.	Selected I	Bond Lengths	(Å) and	Bond Angles	(deg) for	Complexes 5-8

	5	6	7	8
$Zn-N(SiMe_3)_2$	1.9145(16) Å	1.913(3) Å	1.9141(8) Å	1.9037(14) Å
Zn-S _{int}	2.5363(6) Å	2.5428(12) Å	2.5171(16) Å	2.4970(4) Å
Zn-N	2.0379(17) Å	2.030(3) Å	2.0746(18) Å	2.0278(13) Å
Zn-S _{exo}	2.3871(6) Å	2.3930(11) Å	2.3837(6) Å	2.4282(4) Å
C–NMe ₂	1.359(3) Å	1.341(5) Å	1.369(3) Å	1.340(2) Å
S-C	1.785(2) Å	1.785(4) Å	1.801(2) Å	1.7853(16) Å
N-C	1.300(3) Å	1.314(5) Å	1.295(3) Å	1.312(2) Å
S-Zn-N	68.15(5)°	$67.98(11)^{\circ}$	68.55(5)°	$68.68(4)^{\circ}$



Figure 5. Molecular structure of the *bis*-thioureide complexes $[{L^3}Zn]_2$ (9) and $[{L^4}Zn]_2$ (12). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and solvent of crystallization (toluene) associated with 9 have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: 9; -X + 1/2, -Y + 1/2, -Z + 1/2, 12; -X + 1, -Y + 2, -Z + 1.

{ZnSZnS}/{ZnSCN}. The structures resemble the dimeric zinc units found in bis(diethyldithiocarbamates), bis-(diethyldiselenocarbamates), and in mixed alkydialkydithio/ selenocarbamate systems.²⁸ The Zn–N bonds and Zn–S bond distances and angles are similar to those reported here and in related Zn-dithiocarbamate systems.²⁸ The S atoms are engaged in both chelating/bridging interactions, showing significantly longer Zn–S contacts associated with the bridging 3-coordinate S atoms within the {Zn₂S₂} ring [9: 2.8149(7) Å; 12: 2.8061(5) Å] compared to the 2-coordinate S atoms that participate in only a chelating interaction [9: 2.4973(7) Å; 12: 2.3764(6) Å].

While the zinc centers in each complex are 5 coordinate, the geometry about the zinc atoms in **9** is best described as trigonal bypyramidal ($\tau = 0.70$), and distorted square based pyramidal in the case of **12** ($\tau = 0.36$). These distortions arise as a result of (i) the restricted bite distance associated with the chelating ligands [**9**: $62.75(6)^{\circ}$ and $62.75(6)^{\circ}$; **12**: $70.45(5)^{\circ}$ and $63.03(5)^{\circ}$], (ii) the close approach of the dimer forming S atoms [**9**: $2.3645(7)^{\circ}$; **12**: $2.3666(6)^{\circ}$], and (iii) the relative orientation of the isopropyl and mesityl substituents within the two molecules.

Within each $[{L^1}_2Zr]$ unit of complex 9, the two iPr groups on the chelating thioureide ligands are arranged in

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 9 and 12

	9		12
Zn(1)-S(1)	2.8149(7) Å	Zn(1)-S(1)	2.3764(6) Å
Zn(1)-S(2)	2.4973(7) Å	Zn(1)-S(2)	2.8061(5) Å
Zn(1)-S(1)*	2.3645(7) Å	Zn(1)-S(2)*	2.3666(6) Å
Zn(1)-N(11)	2.0199(19) Å	Zn(1)-N(11)	2.0839(15) Å
Zn(1)-N(21)	2.0174(19) Å	Zn(1)-N(21)	2.0198(17) Å
C(11) - N(1)	1.355(3) Å	C(11)-N(1)	1.352(2) Å
S(1)-C(11)	1.773(2) Å	S(1)-C(11)	1.7529(19) Å
N(11)-C(11)	1.303(3) Å	N(11)-C(11)	1.324(3) Å
C(21)-N(2)	1.376(3) Å	C(21)-N(2)	1.350(3) Å
S(2)-C(21)	1.735(2) Å	S(2)-C(21)	1.756(2) Å
N(21)-C(21)	1.315(3) Å	N(21)-C(21)	1.324(2) Å
S(1)-Zn(1)-N(11)	62.75(6)°	S(1)-Zn(1)-N(11)	70.45(5)°
S(2)-Zn(1)-N(21)	69.03(6)°	S(2)-Zn(1)-N(21)	63.03(5)°
S(1)-Zn(1)-S(1)*	84.85(2)°	S(2)-Zn(1)-S(2)*	$89.389(18)^{\circ}$
Zn(1)-S(1)-Zn(1)*	95.15(2)°	Zn(1)-S(2)-Zn(1)*	90.611(18)°

transoidal fashion, with each $[{L^1}_2Zr]$ unit within the dimer then itself arranged *cisoidaly*, resulting in a *trans*-*cis* $[{L^1}_2Zr]_2$ dimer (Figure 6). Contrastingly, in **12**, the two {Mes} groups



Figure 6. Diagram showing the relative orientation of the ${}^{i}Pr$ and ${Mes}$ substituents in the dimers $[{L^{1}}_{2}Zr]_{2}$ (9) and $[{L^{4}}_{2}Zr]_{2}$ (12).

on the thioureide ligands within each $[{L^4}_2Zr]$ unit are arranged in a *cisoidal* fashion about each zinc atom. Each $[{L^4}_2Zr]$ unit within the dimer then arranges itself in a *trans* arrangement resulting in a *cis*-*trans* $[{L^4}_2Zr]_2$ dimer (Figure 6). It should be noted that in the case of 12, the relative displacement of the mesityl groups on the *cis*- $[{L^4}_2Zr]$ unit is such that $\pi-\pi$ stacking is possible with the closest contact between the two approximately parallel {Mes} rings found to be 3.69(8) Å.

Thermal Profiles. The synthesis of Zn(II) *bis*-thioureide compounds has been driven by our interest in the discovery of novel precursors for the MOCVD of ZnS thin films. As such,

thermogravimetric analysis (TGA) was employed to investigate the volatility and thermal stability of complexes 1-12.

Table 5 shows the onset of mass loss, % mass residues, and the expected % mass residue for ZnS from each of the

Table 5. Melting Point, Onset Temperature, Percent
Residual Mass, and Expected Percent Weight for ZnS in
Complexes 1, 2, 4–9, and 12

Compound	Onset Temp. ^a	% Residual mass (Temp.)	Expected % wt for ZnS	
1	160.2 °C	31.3% (440 °C)	43.5%	
2	175.4 °C	33.0% (450 °C)	36.9%	
4	225.8 °C	13.5% (450 °C)	32.3%	
5	180.2 °C	25.9% (360 °C)	26.3%	
6	140.0 °C	25.2% (330 °C)	25.3%	
7	175.3 °C	21.2% (450 °C)	23.7%	
8	225.6 °C	26.0% (475 °C)	21.8%	
9	142.1 °C	21.3% (420 °C)	27.4%	
12	190.5 °C	18.1% (430 °C)	19.2%	
^a Defined as temperature at 1% mass loss.				

synthesized complexes. Because of its polymeric nature, the ^tBu-derivative (3) was not investigated further as a potential ZnS precursor. Similarly, because of the low decomposition temperature of the bis-thioureide complexes 10 and 11, thermogravametric studies were not undertaken.

TG analysis of the methyl zinc thioureide complexes 1 and 2, shows multistep decomposition pathways yielding % residues which are lower than the expected % residue for the formation of ZnS, suggestive of a degree of volatility in the complexes (Figure 7a). In contrast, the mesityl derivative (4) shows a higher degree of thermal stability than that observed for 1 (160.2 °C) and 2 (175.4 °C). In contrast to complexes 1 and 2, the mesityl derivative 4 displays a sharp single step mass loss over a narrow temperature range of (~250-330 °C), resulting in a significantly lower % residual mass than that of ZnS or Zn (13.5% *cf.* 32.2%, 21.7%, respectively) suggestive of a significantly high degree of volatilization.

For the zinc amide complexes 5-8, the thermal decomposition processes were all found to be multistep, displaying rapid mass loss in the initial phase, tapering off over a wide



Figure 7. Thermogravimetric plots for complexes 1, 2, and 4 (a), 5-8 (b), and 9 and 12 (c). (5 °C min^{-1} , 20 mL min⁻¹ N₂ flow).

temperature range (Figure 7b) to reach mass residues which are all close to the expected values for the formation of ZnS, with the exception of the ^tBu derivative (7) which is fractionally lower.

For the bis-thioureides 9 and 12, the TGA plots (Figure 7c) clearly display two complexes which, while both displaying a single mass loss event, display very different thermal stabilities. For the isopropyl derivative 9, mass loss begins at ~142 °C, whereas, for the mesityl derivative 12, mass loss only occurs at ~190 °C (*cf.* 225.8 °C for $[{L^4}ZnMe]_2$ (4) and 225.6 °C for $[{L^4}Zn(N(SiMe_3)_2)]_2$ (8)). In both instances, the resulting % residual masses (21.3 and 18.1 wt %, respectively) are lower than that expected for the formation of ZnS (27.4 and 19.4 wt %, respectively). In an attempt to ascertain possible decomposition pathways for precursors 9, TGA-coupled

mass spectrometry was undertaken. Unfortunately TGA-MS experiments did not yield conclusive results with respect to precursor decomposition pathways: Peaks at m/z = 45 amu and m/z = 101.1 amu were observed in the mass spectra which we attribute to formation of dimethylamine and isopropyl isothiocyanate, respectively, suggestive of a deinsertion pathway. We suggest that these results provide strong further support for the generalized assumption that thioureide ligands are potentially significant ligands for the development of stable metal sulfide precursors.

Thin Film Deposition. The low onset temperature for the decomposition of compound 9 (\sim 142 °C), in conjunction with ease of synthesis, stability, and reasonable solubility in THF, led us to assess its viability as a low temperature single source precursor for the AACVD of ZnS thin films. As part of a preliminary viability study, films were deposited under hot wall conditions in a previously described CVD reactor^{19,21,22,24} onto silica-coated float glass substrates (Pilkington NSG Ltd.). The deposition conditions are shown in Table 6. The films

Table 6. Deposition Conditions Used for the AACVD of ZnS Thin Films with Compound 9

Film	Conc (mol dm^{-3})	Substrate Temp (°C)	Deposition Time (min)
Α	0.15	150	60
В	0.15	200	60
С	0.15	250	60
D	0.15	300	60

were deposited from 0.15 M solutions of 9 in THF (optimized) onto (100) silicon wafers and glass substrates, at temperatures of 150, 200, 250, and 300 $^{\circ}$ C for films A–D, respectively.

The films (A-D) were primarily transparent in appearance with more visually yellow material at the leading edge of the substrate, which could indicate the presence of S rich ZnS. At the lower deposition temperatures (150 and 200 °C), films **A** and **B** appeared to be very thin and slightly opaque with a very slight yellow appearance. Higher temperatures, however, delivered significantly improved coverage of the substrate to provide films that were transparent.

The films (A-D) were air and water stable, showing no observable change (as determined by powder X-ray diffraction (PXRD) and UV–vis transmission spectroscopy) over a period of 2 months. The films were insoluble in common organic solvents but were quickly decomposed in dilute nitric acid and bleach, yielding H₂S.

Films C and D, deposited at 250 and 300 °C, respectively, appeared transparent with slight yellowing at the leading edge of the substrate. The mechanical integrity of the as-deposited thin films was assessed using the "Scotch Tape test".²⁹ The Scotch tape test resulted in no obvious removal of material from the films C and D; however, some material was removed from the surface of films A and B, suggesting less well adhered films. PXRD analysis was performed on all the deposited films to determine the crystallinity of the materials. Similar analysis of the slightly yellow regions of the films yielded analogous results. Representative PXRD patterns for the films C and D are shown in Figure 8.

Films A and B, deposited at 150 and 200 $^{\circ}$ C respectively, were found to be amorphous within the limits of the instrument. Films C and D, deposited at 250 and 300 $^{\circ}$ C respectively, provided clear indication of crystallinity with one



Figure 8. (a) PXRD patterns of films **C**–**D** resulting from AACVD with compound 9, (b) Raman spectra of films **C**–**D**.

high intensity maximum, which could be readily indexed to the (002) reflection of W-ZnS (JCPDS 36-1450), indicative of ZnS films of polycrystalline nature with a hexagonal closepacked structure. The reflection corresponding to the (002) planes increased in intensity for films deposited at higher temperature. For film D, broader peaks also present in the PXRD pattern could be indexed to the (100), (101), (102), (110), (103), and (112) reflections of W-ZnS. For the ZnS films C and D, PXRD suggests that crystallites are preferentially oriented with (002) planes parallel to the substrate surface, with the c-axis of the hexagonal cell normal to the substrate. In order to obtain more structural information, the mean crystallite size (D) of the films was calculated using the Debye-Scherrer formula. For films C and **D** the minimum domains in the (00L) dimension, calculated from X-ray line broadening using the (002) peak, were found to be 9.4 and 25.0 nm, respectively, such that the films deposited at higher temperatures were characterized by greater crystallite size. Experimentally, the 2θ positions corresponding to the (002) direction changed from 27.9° to 28.8° as the deposition temperature was increased from 250 °C, C, to 300 °C, D. A simple calculation confirmed that the lattice constants of the c-axes for both films were close to and within experimental error of the reported lattice parameter for W-ZnS (6.402(8) Å).³⁰

The Raman spectra of the crystalline films C and D (Figure 8) displayed absorptions at 275 (TO), 335 (SO), 402 (TA + TO), 614 (2TO), and 684 (2LO) cm⁻¹. These vibrations correspond with those reported for W-ZnS in the literature.³¹ In both the PXRD and Raman spectra, no peaks from any impurities such as ZnO or other compounds are detected.

Deposition temperature, as well as choice of precursor, clearly has an effect on the morphology, crystallite size, and film thickness of the as deposited thin films. The role of the carrier solvents has also previously been seen to influence the morphology of the films (e.g., tungsten oxide³² and tin oxide³³), and is generally attributed to concentration effects, chemical effects, and modulation of the rates of deposition and droplet evaporation. The latter of these effects is more likely the dominant here for solvents such as toluene and THF, which do not form reactive radical species at the temperatures used in our experiments. Attempts to increase the concentration of precursor and change the carrier solvent from THF to toluene were met with varying degrees of success. Initial investigations of precursor concentrations >0.15 M (in THF) resulted in inconsistent thin film deposition at 300 °C. The reduced solubility of complex 9 in toluene also resulted in uneven film growth from 0.1 M solutions of 9 in toluene.

Atomic force microscopy (AFM) (ESI) was performed to determine the root-mean-square (rms) surface roughness of the ZnS thin films (Table 7). In all cases, films A-D were

Table 7. Structural Characteristics of ZnS Thin Films

	Roughness	Film	Average	
	Values	Thickness	Crystallite size	Lattice parameter
Film	$(nm)^a$	$(d) (nm)^{b}$	(D) (nm)	(Å) (c)
Α	2.63	53.83		
В	6.54	61.52		
С	7.02	339.88	9.38	$6.39 (2\Theta = 27.9^{\circ})$
D	14.59	443.96	24.97	$6.19 (2\Theta = 28.8^{\circ})$
^a As de	etermined fro	om AFM over	three positions.	^b As determined by
SEM.			-	

relatively smooth and were consistent with our observation that with increasing deposition temperature there was an attendant increase in crystallite size, such that films A and B were significantly less crystalline, with RMS values of 2.6 and 6.5 nm respectively, compared to the more crystalline thin films C and D (RMS values of 7.0 and 14.6 nm).

Figure 9 displays images obtained from field emission scanning electron microscopy (FESEM), which was carried out to determine the morphology of the films. The plan view of films C and D (Figure 9a and 9c) and the cross-sectional image (Figure 9b and 9d) both illustrate that the thin films comprise a collection of densely packed crystallites that are globular in appearance. For film D these crystallites (Figure 9c) are significantly larger (30–70 nm) than those observed in film C (40–50 nm). This trend is also observed in films A and B, where crystallite size decreases in line with deposition temperature and is consistent with the PXRD and AFM data. For films A and B FE-SEM images are shown in the Supporting Information.

Energy dispersive X-ray (EDX) measurements revealed the presence of Zn and S in all thin films deposited. Films deposited at 150 °C (**A**) displayed a relative ratio of Zn:S of 1:1.05, close to the ideal 1:1 ratio, while films deposited at higher temperatures, *i.e.* 200 °C (**B**), 250 °C (**C**), and 300 °C (**D**) all appear to be sulfur rich with Zn/S ratios of 1.47, 1.41, and 1.39, respectively, consistent with Zn/S ratios of p-type (Srich) ZnS.³⁴ While it is possible that these films could be more accurately described as cocrystalline ZnS with additional S, there is no evidence of the presence of crystalline or amorphous sulfur from PXRD or Raman spectroscopy analysis.



Figure 9. FE-SEM images of AACVD ZnS films from compound 9: (a) plan view of film C (250 °C); (b) cross-sectional view of film C (250 °C); (c) plan view of film D (300 °C); (d) cross-sectional view of film D (300 °C).



Figure 10. (a) UV-vis transmission plots of films A-D (150 °C, 200 °C, 250 °C, and 300 °C, respectively) resulting from AACVD with compound 9, (b) Tauc plots of films A-D.

The room temperature UV-vis absorption spectra of the ZnS samples in the wavelength range 400–850 nm were recorded. All films displayed good visible light transmission, with optical transmission ($\lambda = 400-700 \text{ nm}$) $\geq 75\%$ in all cases. Band gap energies were estimated to lie in the range 3.71 to 3.79 eV from representative Tauc plots (Figure 10). These observations are commensurate with the films behaving as the bulk semiconductor, with direct band gaps similar to those reported elsewhere in the literature for ZnS.³⁵

CONCLUSIONS

A family of zinc thioureide systems have been described and their potential for the deposition of thin films of ZnS by AACVD has been explored. The homoleptic precursor, $[{L^1}_2Zn]_2$ (9) bearing the isopropyl-thiouride ligand was used to deposit ZnS films in the temperature range 150–300 °C, with hexagonal (Wurtzite) W-ZnS deposited at temperatures of 250 °C and above, as identified by PXRD and Raman spectroscopy. EDX analysis confirmed the deposition of ZnS over the entire temperature range with the manifestation of S-

rich films at higher temperatures. Optical analysis of the thin films shows high optical transmission and band gap estimations of between 3.17 and 3.79 eV. This study builds on our work, described elsewhere,²² on the efficacy of thioureide systems as a novel class of precursor for the deposition of metal sulfide thin films. In contrast to our previous study²² into Sn(II) thioureide systems in which the control of the deposition temperature has a direct effect on the phase of SnS deposited (α or π), no such control is observed here, and no obvious correlation between precursor structure and phase of ZnS deposited can be discerned. Further work on the structure– reactivity relationships of metal thioureide complexes for the deposition of a range of metal sulfide thin films is ongoing.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried over activated alumina columns using an Innovative Technology solvent purification system (SPS) and degassed under an argon atmosphere. $Zn(N(SiMe_3)_2)_2$ was produced according to literature

procedures,³⁶ and all other reagents were purchased from commercial sources.

Elemental analyses were performed externally by London Metropolitan University Elemental Analysis Service, UK. ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were recorded on Bruker Advance 300 or 500 MHz FT-NMR spectrometers, as appropriate, in C_6D_6 at room temperature. Chemical shifts are given in ppm with respect to Me₄Si (¹H, ¹³C). UV–vis spectra were recorded using a PerkinElmer LAMBDA 750/650 UV/vis/near-IR spectrophotometer. Measurements were recorded at 1400 to 400 nm and zero referenced using 5 mm high-grade Pilkington-NSG float-glass substrates. The measurements were recorded at 1 nm increments.

Synthesis of the Pro-ligand [ⁱ**PrN(H)CSNMe**₂] (**HL**¹). In a dry round-bottom flask under nitrogen, dimethylamine was bubbled through a colorless solution of isopropyl isothiocyanate (4.23g, 30 mmol) in hexane (100 mL) at 0 °C yielding a white precipitate. The product was extracted from solution by filtration and washed with hexane. Yield 3.69 g (84%), (mp 75–77 °C). ¹H NMR (500 MHz, C_6H_6) $\delta_{\rm H}$: 0.99 (m, 6H (CH<u>Me</u>₂), 2.52 (s, 6H, N<u>Me</u>₂), 4.42 (br s, 1H, N(<u>H</u>)), 4.87 (m, 1H, C<u>H</u>Me₂); ¹³C{¹H} NMR (125.7 MHz, C₆D₆) $\delta_{\rm C}$; 22.9 (CH(<u>CH</u>₃)₂), 39.4 (N<u>Me</u>₂), 47.3 (<u>C</u>H(CH₃)₂), 182.1 (<u>C</u>= S); Elemental analysis (expected): C 49.31% (49.28%); H 9.62%, (9.65%); N 19.18% (19.15%)

Synthesis of the Pro-ligands $[CyN(H)CSNMe_2]$ (HL²), [^tBuN-(H)CSNMe₂] (HL³) and [MesN(H)CSNMe₂] (HL⁴). The pro-ligands HL²-HL⁴ were made in an analogous manner to HL¹ using of 5.59g (30 mmol) cyclohexyl isothiocyanate, 4.81g (30 mmol) of tertiary-butyl isothiocyanate and 5.32g (30 mmol) of 2,4,6-trimethylphenyl isothiocyanate, respectively.

HL²: Yield: 4.8¹g (86%) (mp 91–93 °C). ¹H NMR (500 MHz, C₆D₆): $\delta_{\rm H}$ 0.85–1.06 (m, 3H, C<u>H</u>₂), 1.20–1.32 (m, 2H, C<u>H</u>₂), 1.42–1.48 (m, 1H, C<u>H</u>₂), 1.49–1.57 (m, 2H, 6H, C<u>H</u>₂), 2.08–2.15 (m, 2H, C<u>H</u>₂), 2.63(br s, 6H, N<u>Me</u>₂), 4.64 (br m, 1H, NC(<u>H</u>)) 4.73 (br S, 1H, N(<u>H</u>)); ¹³C{¹H} NMR (125.7 MHz, C₆D₆); $\delta_{\rm C}$ 25.4 (<u>C</u>H₂), 26.1 (<u>C</u>H₂), 33.5 (<u>C</u>H₂), 39.5 (<u>C</u>H₃), 54.3 (<u>C</u>H), 181.9 (<u>C</u>=S); Elemental analysis (expected): C 58.02% (58.02%), H 9.78% (9.74%), N 15.08% (15.04%).

HL³: Yield: 3.89g (81%) (mp 57–58 °C). ¹H NMR (500 MHz, C₆D₆) $\delta_{\rm H}$ 1.51 (s, 9H, C<u>Me₃</u>), 2.60, (s, 6H, N<u>Me₂</u>), 4.72 (bs s, 1H, N(<u>H</u>)); ¹³C{¹H} NMR (125.7 MHz, C₆D₆) $\delta_{\rm C}$ 29.3 (C<u>Me₃</u>), 39.6 (N<u>Me₂</u>), 53.7 (<u>C</u>Me₃), 181.7 (<u>C</u>=S); Elemental analysis (expected): C 52.59% (52.46%), H 10.09% (10.06%), N 17.51% (17.48%).

HL⁴: Yield: 5.47g (82%); (177–180 °C) ¹H NMR (500 MHz, C_6D_6) δ_H 2.17 (s, 3H, para-C<u>Me_3</u>), 2.20 (s, 6H, ortho-C<u>Me_3</u>), 2.64 (s, 6H N<u>Me_2</u>), 5.64 (br s, 1H, N(<u>H</u>)), 6.82 (s, 2H, Ar–C<u>H</u>); ¹³C{¹H} NMR (125.7 MHz, C_6D_6) δ_C ; 18.6 (ortho-<u>MeH_3</u>) 21.1 (para-<u>Me</u>), 40.2 (N<u>Me_2</u>), 129.2 (Ar-<u>C</u>H), 135.7 (Ar-<u>C</u>), 136.5 (Ar-<u>C</u>), 136.7 (Ar-<u>C</u>), 183.0 (<u>C</u>=S); Elemental analysis (expected): C 64.82% (64.83%), H 8.16% (8.16%), N 12.60% (12.58%).

Synthesis of [{ⁱPrNC(S)NMe₂}ZnMe]₂([{L¹}ZnMe]₂) (1). To a cooled solution of HL¹ (0.197g, 1.35 mmol) in 20 mL of toluene was added 0.675 mL (1.35 mmol) of a 2.0 M dimethyl zinc solution in toluene and the resulting reaction mixture was left to stir overnight. Visible gas was seen to be produced in the colorless solution. The solution was reduced *in vacuo* and recrystallized at -28 °C affording white crystals. Yield: 0.13 g (43%). ¹H NMR (500 MHz, C₆D₆): $\delta_{\rm H}$ -0.01 (s, 3H, Zn-CH₃), 1.03 (d, J = 6.20 Hz, 6H, -NCHMe₂), 2.58 (s, 6H, -NMe₂), 3.50 (sept, J = 6.20 Hz, 1H, -NCHMe₂); ¹³C{¹H} NMR (125.7 MHz, C₆D₆): $\delta_{\rm c}$ -11.9 (Zn-Me₂), 25.0 (NCHMe₂), 42.9 (-CNMe₂), 49.8 (NCHMe₂), 173.0 (S-C-NMe₂); Elemental analysis for C₁₄H₃₂N₄S₂Zn₂ (expected): C 37.19% (37.26%), H 7.17% (7.15%), N 12.39% (12.41%).

Synthesis of $[{CyNC(S)NMe_2}ZnMe]_2([{L^2}ZnMe]_2)$ (2), $[{^{t}BuNC(S)NMe_2}ZnMe]_{\infty}([{L^3}ZnMe]_{\infty})$ (3) and $[{MesNC(S)-NMe_2}ZnMe]_2([{L^4}ZnMe]_2)$ (4). The complexes 2–4 were made in an analogous manner to 1 using of 0.186g, (1 mmol) of HL², 0.139g (1 mmol) of HL³ and 0.22g (1 mmol) of HL⁴ respectively.

2: Yield: 0.08 g (29%). ¹H NMR (500 MHz, C₆D₆): $\delta_{\rm H}$ 0.05 (s, 3H, Zn-<u>Me</u>), 1.08–0.91 (m, 2H, Cy-C<u>H₂</u>), 1.46–1.35 (m, 2H, Cy-C<u>H₂</u>), 1.60–1.49 (m, 2H, Cy-C<u>H₂</u>), 1.87–1.75 (m, 2H, Cy-C<u>H₂</u>), 2.63 (s,

6H, $-N\underline{M}_{\mathfrak{E}_2}$), 3.25–3.19 (br m, 1H, $-NC\underline{H}(Cy)$); $^{13}C{^1H}$ NMR (125.7 MHz, C_6D_6): $\delta_C -11.8$ (Zn- $\underline{M}_{\mathfrak{E}}$), 25.6 (Cy- $\underline{C}H_2$), 25.8 (Cy- $\underline{C}H_2$), 36.0 (Cy- $\underline{C}H_2$), 43.0 ($-N\underline{M}_{\mathfrak{E}_2}$), 58.5 ($-N\underline{C}HCy$), 173.0 (S- $\underline{C}-NMe_2$); Elemental analysis for $C_{20}H_{40}N_4S_2Zn_2$ (expected): C 45.18% (45.20%), H 7.58% (7.59%), N 10.54% (10.54%).

3: Yield: 0.22 g (93%). ¹H NMR (500 MHz, C_6D_6): δ_H 0.01 (s, 3H, Zn-<u>Me</u>), 1.22 (s, 9H, -NC<u>Me_3</u>), 2.47 (s, 6H, -N<u>Me_2</u>); ¹³C{¹H} NMR (125.7 MHz, C_6D_6) δ_C -11.5 (Zn-<u>Me</u>), 31.0 (-N<u>C</u>Me₃), 44.4 (-NMe₂), 55.4 (-N<u>C</u>Me₃), 181.9 (S-<u>C</u>-NMe₂); Elemental analysis for C₁₆H₃₆N₄S₂Zn₂ (expected): C 39.98% (40.09%), H 7.60% (7.57%), N 11.68%, (11.69%).

4: Yield: 0.31 g, (99%). ¹H NMR (500 MHz, C₆D₆): $\delta_{\rm H}$ 0.41 (br s, 3H, Zn-<u>Me</u>), 2.06 (s, 6H, ortho-<u>Me</u>), 2.15 (s, 3H, para-<u>Me</u>), 2.42 (s, 6H, -NMe₂), 6.61 (s, 2H, Ar-C<u>H</u>); ¹³C{¹H} NMR (125.7 MHz, C₆D₆): $\delta^{\rm C}$ -10.4 (Zn-<u>Me</u>), 19.0 (ortho-<u>Me</u>), 20.9 (para-<u>Me</u>), 42.0 (-NMe₂), 131.8 (ortho-<u>C</u>Me), 132.4 (para-<u>C</u>Me), 144.2 (-N-<u>C</u>), 178.0 (S-<u>C</u>-NMe₂); Elemental analysis for C₂₆H₄₀N₄S₂Zn₂ (expected): C 51.69%, (51.74%), H 6.65% (6.68%), N 9.28% (9.28%).

Synthesis of [{ⁱPrNC(S)NMe₂}Zn{N(SiMe₃)₂}]₂([{L¹}Zn{N-(SiMe₃)₂}]₂) (5). A cooled solution of Zn{N(SiMe₃)₂} (0.39g, 1 mmol) dissolved in toluene, was combined with a solution of the pro ligand HL¹ (0.146g, 1 mmol) in toluene (20 mL), and allowed to stir for 8h. *In vacuo* removal of solvent resulted in the formation of a cloudy suspension, which was resolved with gentle heating, and allowed to crystallize at -28 °C affording white crystals. Yield: 0.25 g (67%). ¹H NMR (500 MHz, C₆D₆) $\delta_{\rm H}$ 0.46 (s, 18H, Zn–N(Si<u>Me₃)₂</u>) 1.20–1.13 (m, 6H, -NCH<u>Me₂</u>), 2.63 (s, 6H, -N<u>Me₂</u>), 3.62–3.53 (m, 1H, -NC<u>H</u>Me₂); ¹³C{¹H} NMR (125.7 MHz, C₆D₆): $\delta_{\rm C}$ 6.4 (Zn–N(Si<u>Me₃)₂), 24.9 (-NCHMe₂), 43.6 (-NMe₂), 50.9 (-NCHMe₂), 186.1 (S-C-NMe₂); Elemental analysis for C₂₄H₆₂N₆S₂Si₄Zn₂ (expected): C 38.37% (38.85%), H 8.38%, (8.42%), N 11.35% (11.33%).</u>

Synthesis of $[\{CyNC(S)NMe_2\}Zn\{N(SiMe_3)_2\}]_2([\{L^2\}ZnN\{N(SiMe_3)_2\}]_2)$ (6), $[\{^{t}BuNC(S)NMe_2\}ZnN\{N(SiMe_3)_2\}]_2([\{L^3\}ZnN\{N(SiMe_3)_2\}]_2)$ (7) and $[\{MesNC(S)NMe_2\}ZnN\{N(SiMe_3)_2\}]_2([\{L^4\}ZnN\{N(SiMe_3)_2\}]_2)$ (8). The complexes 6–8 were made in an analogous manner to 5 using of 0.186g, (1 mmol) of HL², 0.139g (1 mmol) of HL³ and 0.22g (1 mmol) of HL⁴ respectively.

6: Yield: 0.29 g (70%). ¹H NMR (500 MHz, C_6D_6) δ_H 0.48 (s, 3H, Zn-N(Si(<u>Me_3</u>)₂), 1.13–1.03 (m, 2H, Cy-C<u>H</u>₂), 1.51–1.45 (m, 2H, Cy-C<u>H</u>₂), 1.70–1.60 (m, 2H, Cy-C<u>H</u>₂), 1.91–1.815 (m, 2H, Cy-C<u>H</u>₂), 2.67 (s, 6H, -N<u>Me</u>₂), 3.33–3.22 (m, 1H, -NC<u>H</u>Cy); ¹³C{¹H} NMR (125.7 MHz, C_6D_6) δ_C 6.7 (Zn–N(Si<u>Me</u>₃), 25.6 (Cy-<u>C</u>H₂), 25.7 (Cy-<u>C</u>H₂), 35.9 (Cy-<u>C</u>H₂), 43.6 (-N<u>Me</u>₂), 59.0 (-N<u>C</u>HCy), 179.2 (S-<u>C</u>-NMe₂); Elemental analysis for C₃₀H₇₀N₆S₂Si₄Zn₂ (expected): C 43.86%, (43.83%), H 8.53% (8.58%), N 10.32% (10.22%).

7: Yield: 0.16 g (42%); ¹H NMR (500 MHz, C_6D_6): δ_H 0.44 (s, 18H, Zn-N(Si<u>Me_3</u>)₂), 1.31 (s, 9H, -NC<u>Me_3</u>), 2.52 (s, 6H, -N(C<u>H_3</u>)₂); ¹³C{¹H} NMR (125.7 MHz, C_6D_6): δ_C 6.6 (Zn-N(Si<u>Me_3</u>), 31.1 (-NC<u>Me_3</u>), 44.7 (-N<u>Me_2</u>), 57.9 (-N<u>C</u>Me_3), 179.1 (S-<u>C</u>-NMe₂); Elemental analysis for $C_{26}H_{66}N_6S_2Si_4Zn_2$ (expected): C 39.96%, (40.55%), H 8.69% (8.64%), N 10.98% (10.91%).

8: Yield: 0.23 g (52%); ¹H NMR (500 MHz, C_6D_6) δ_H 0.31 (s, 18H, -N(Si<u>Me_3</u>)₂), 2.09 (s, 3H, para-<u>Me</u>), 2.35 (s, 6H, ortho-<u>Me</u>), 2.58 (s, 6H, -N<u>Me_2</u>), 6.73 (s, 2H, meta-C<u>H</u>); ¹³C{¹H} NMR (125.7 MHz, C₆D₆) δ_C 6.0 (-N(Si<u>Me_3</u>)₂), 19.4 (ortho-<u>Me</u>), 20.9 (para-<u>Me</u>), 42.9 (-N<u>Me_2</u>), 128.9 (meta-<u>C</u>H), 134.2 (para-<u>C</u>-Me), 143.5 (ortho-<u>C</u>-Me), 144.3 (-N-<u>C</u>), 168.4 (S-<u>C</u>-NMe₂); Elemental analysis for C₃₆H₇₀N₆S₂Si₄Zn₂ (expected): C 48.87%, (48.83%), H 7.86% (7.89%), N 9.57% (9.40%).

Synthesis of *Bis*-[{ⁱPrNC(S)NMe₂}₂Zn]₂([{L¹}₂Zn]₂) (9). Zn{N(SiMe₃)₂}₂ (0.39g, 1 mmol) was dissolved in toluene (20 mL) and added to a cooled solution of the pro-ligand HL¹ (0.292g, 2 mmol) in 20 mL of toluene, and stirred for 8 h. The volume of solvent was reduced by half, *in vacuo*, yielding a cloudy suspension which was redissolved with gentle heating, and allowed to crystallize at -28 °C, affording white crystals. Yield; 0.21g (60%). ¹H NMR (300 MHz, C₆D₆) $\delta_{\rm H}$ 1.21 (m, 6H, -NCH<u>Me₂</u>), 2.64 (s, 6H, -N<u>Me₂</u>), 3.63 (m, 1H, -NC<u>H</u>Me₂); ¹³C{¹H} NMR (75.5 MHz, C₆D₆) $\delta_{\rm C}$ 25. Eight

(-NCH<u>Me₂</u>), 43.98 (-N<u>Me₂</u>), 50.9 (-N<u>C</u>H(CH₃)₂), 181.0 (S-<u>C</u>-NMe₂); Elemental analysis for C₂₄H₅₂N₈S₄Zn₂:C₇H₈ (expected): C 46.33%, (46.32%), H 7.50% (7.52%), N 14.13% (13.94%).

Synthesis of Bis-[{CyNC(S)NMe₂}₂Zn]([{L²}₂Zn]) (10), Bis-[{^tBuNC(S)NMe₂}₂Zn]₂([{L³}₂Zn]₂) (11) and Bis-[{MesNC(S)- $NMe_{2}Zn_{2}([{L^{4}}Zn_{2}])$ (12). The complexes 10–12 were made in an analogous manner to 9 using of 0.186 g, (1 mmol) of HL², 0.139 g (1 mmol) of HL³ and 0.22 g (1 mmol) of HL⁴ respectively.

10: Yield 0.25 g (56%); ¹H NMR (500 MHz, C_6D_6) δ_H 1.17–1.03 $(m, 3H, Cy-CH_2)$ 1.51–1.41 $(m, 1H, Cy-CH_2)$, 1.71–1.57 $(m, 2H, CH_2)$ Cy -CH₂), 2.16-1.02 (m, 2H, Cy-CH₂), 2.65 (s, 6H, -NMe₂), 3.35-3.23 (m, 1H, -N-C<u>H</u>(Cy)); ¹³C{¹H} NMR (125.7 MHz, C₆D₆) $\delta_{\rm C} 25.8 \, ({\rm Cy-}\underline{C}{\rm H}_2), \, 36.1 \, ({\rm Cy-}\underline{C}{\rm H}_2), \, 43.4 \, (-{\rm N}\underline{M}\underline{e}_2), \, 58.3 \, (-{\rm N}\underline{C}), \, 181.5$ (S-C-NMe₂); Elemental analysis for C₃₆H₆₈N₈S₄Zn₂ (expected): C 49.49% (49.59%), H 8.01% (7.86%), N 12.79% (12.85%).

11: Yield 0.32g (83%); ¹H NMR (500 MHz, C₆D₆) $\delta_{\rm H}$ 1.22 (s, 9H, -NC<u>Me₃</u>), 2.47 (s, 6H, -N<u>Me₂</u>); ${}^{13}C{}^{1}H{}$ NMR (125.7 MHz, C₆D₆) $\delta_{\rm C}$ 31.0 (-NC<u>Me_3</u>), 44.4, (-N<u>Me_2</u>), 65.3 (-N<u>C</u>Me₃), 182.0 (S-<u>C</u>-NMe₂); Elemental analysis for C₂₈H₆₀N₈S₄Zn₂(expected): C 43.48% (43.80%), H 7.86% (7.88%), N 14.57% (14.59%).

12: 0.41g, (80%) ¹H NMR (500 MHz, C_6D_6) δ_H 2.06 (s, 6H, ortho-Me), 2.16 (s, 3H, (para-Me), 2.42 (s, 6H, -NMe2), 6.65 (s, 2H, Ar-C<u>H</u>); ¹³C{¹H} NMR (125.7 MHz, C₆D₆) $\delta_{\rm C}$ 19.0 (ortho-<u>Me</u>), 20.9 (para-Me), 42.0 (-NMe2), 110.4 (ortho-CMe), 128.5 (Ar-CH), 132.1 (para-C-Me), 144.2 (-NC(Ar)), 177.6 (S-C-NMe2); Elemental analysis for C48H68N8S4Zn2 (expected): C 56.71% (56.74%), H 6.86%, (6.75%), N 10.87% (11.03%).

Single Crystal X-ray Diffraction Studies. Experimental details relating to the single-crystal X-ray crystallographic studies for compounds 1-9 and 12 are summarized in Table S1 (ESI). Single crystal X-ray crystallography data were collected at 150 K on RIGAKU SuperNova Dual wavelength diffractometer equipped with an Oxford Cryostream, featuring a micro source with MoK α radiation $(\lambda = 0.71073 \text{ Å})$ and Cu K α radiation $(\lambda = 1.5418 \text{ Å})$. Crystals were isolated from an argon filled Schlenk flask and immersed under oil before being mounted onto the diffractometer. Structures were solved by direct methods throughout and refined on F² data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealized positions and refined using the riding model. Refinements were straightforward with no additional points that merit note. CCDC 1881545-1881554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

AACVD Experiments. Thin films were deposited using a horizontal hot wall reactor. The aerosol was generated with a TSI 3076 Constant Output Atomiser using N₂ at 20 psi to generate the aerosol and act as the carrier gas. Films were grown on either 2.5 cm \times 15 cm SiO₂-coated glass (Pilkington NSG Ltd.), which were cleaned with isopropanol, water, and acetone and then dried under a flow of nitrogen gas, or commercial crystalline silicon. For each deposition a 0.15 M THF solution of 9 was made up in a glovebox, and transferred into a bubbler under an inert atmosphere. Depositions were carried out at 200, 250, 300, and 350 °C for 1 h using N2 as a carrier gas.

The precursor solution was prepared within a glovebox under an atmosphere of argon and all solvents were dried and degassed prior to use. The precursor bubbler was kept under an atmosphere of argon, sealed, and attached onto to the AACVD apparatus. Once all substrates were prepared and mounted into the deposition chamber, nitrogen gas was allowed to flow through the system, bypassing the precursor holder, for 20 min in order to purge the system with nitrogen. Then with continuing gas flow the hot-wall furnace is switched on and allowed to reach the target deposition temperature and equilibrate for 20 min. Once this is achieved the gas flow is diverted to flow via the precursor solution which draws the solution into the TSI 3076 Constant Output Atomiser and out into the deposition chamber where the deposition commences and the timer is

started. Gas flow is monitored via bubbler and gas pressure fixed 10 bar until it reaches the atomizer, as described previously.^{19,21,22,2}

Thermogravimetric Analysis (TGA). TGA was collected using a TGA 4000 PerkinElmer system. Samples were prepared air sensitively using a crimped aluminum sample pan. TGA was performed under a flow of N₂ at 20 mL min⁻¹ and heated from 30 to 600 °C at a ramp rate of 5 °C min⁻¹. TGA-MS was performed under argon (20 mL/ min) at a ramp rate of 5 °C/min between 30 and 600 °C on a Setaram Setsys Evolution TGA 16/18 with the evolved gases passing through a Pfeiffer Vacuum Omnistar GSD 320 quadrapole mass spectrometer. Samples were contained in alumina crucibles. Experiments were performed by MC², University of Bath, UK, and results were analyzed using Excel.

Powder X-ray Diffractometry (PXRD). PXRD data was collected on a BRUKER D8-Advance. The X-ray diffraction spectra were collected for the thin films using the flat plate mode from 5 to 70 2θ at 2° per minute. X-rays were generated from a Cu source at wavelengths of 1.54 Å.

Scanning Electron Microscopy (SEM). SEM was performed to visualize the morphology of the films as both cross sections (using a Field Emission Scanning Electron Microscope 6301F) and top down (JEOL 6480 Low Vacuum large stage SEM platform) images. The films were prepared by mounting onto steel SEM mounts with conductive carbon tape attached to the bottom and top surface of the films, to maximize conductivity of electrons and prevent charge accumulation. Samples were desiccated at 35 °C for 24 h prior to analysis.

Atomic Force Microscopy (AFM). AFM analysis was performed using a Digital Instruments Nanoscope IIIa, with BRUKER SNL-10 Silicon on Nitride Lever contact tips (tip radius <10 nm, f_0 : 50–80 kHz, k: 0.350 N/m and T: 600 nm), in contact mode. Images were processed using the open access Gwyddion SPM data analyzer.

Energy Dispersive X-ray Spectroscopy (EDS). EDS was performed using an Oxford Instruments Scanning Electron Microscope 6480 LV and processed on INCA Wave software. All spectra were standardized and calibrated against a standard silicon wafer sample. The magnification, working distance, and beam energy (10 keV) were kept consistent between spectral analyses.

Raman Spectroscopy. Raman spectra were collected using a Renishaw inVia Raman Microscope fitted with a 532 nm laser at a 10% spot size, 3 s exposure time, and 1% energy intensity. The data was processed using a Renishaw WiRE software package.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b03363.

Figures showing the molecular structures of complexes 5, 6, and 8. Experimental details relating to the singlecrystal X-ray crystallographic studies and crystallographic data for complexes 1-9 and 12. Additional FE-SEM and AFM images of thin films (PDF)

Accession Codes

CCDC 1881545-1881554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: a.l.johnson@bath.ac.uk. ORCID © Michael S. Hill: 0000-0001-9784-9649 Andrew L. Johnson: 0000-0001-5241-0878

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the EPSRC for funding (EP/L016354/1), the EPSRC Centre for Doctoral Training in Sustainable Chemical Technologies for a PhD studentship (H.S.I.S.), the University of Bath for financial support (PhD studentship to J.D.P.), and the Royal Thai Government for a postgraduate scholarship (P.T.).

REFERENCES

(1) (a) Yanagiya, S.-i.; Iseki, Y.; Kaito, T.; Mori, A.; Kaito, C.; Sekiguchi, T.; Inoue, T. Growth of ZnS Nano-Crystallites in Gel and their Characterization. *Mater. Chem. Phys.* **2007**, *105*, 250–252. (b) Fang, X.; Bando, Y.; Gautam, U. K.; Zhai, T.; Zeng, H.; Xu, X.; Liao, M.; Golberg, D. ZnO and ZnS Nanostructures: Ultraviolet-Light Emitters, Lasers, and Sensors. *Crit. Rev. Solid State Mater. Sci.* **2009**, *34*, 190–223. (c) Fang, X.; Zhai, T.; Gautam, U. K.; Li, L.; Wu, L.; Bando, Y.; Golberg, D. ZnS Nanostructures: From Synthesis to Applications. *Prog. Mater. Sci.* **2011**, *56*, 175–287. (d) Ehsan, M. A.; Peiris, T. A. N.; Wijayantha, K. G. U.; Khaledi, H.; Ming, H. N.; Misran, M.; Arifin, Z.; Mazhar, M. Surface Morphological and Photoelectrochemical Studies of ZnS Thin Films Developed from Single Source Precursors by Aerosol Assisted Chemical Vapour Deposition. *Thin Solid Films* **2013**, *540*, 1–9.

(2) Yeh, C.-Y.; Lu, Z. W.; Froyen, S.; Zunger, A. Zinc-Blende– Wurtzite Polytypism in Semiconductors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 10086–10097.

(3) La Porta, F. A.; Gracia, L.; Andrés, J.; Sambrano, J. R.; Varela, J. A.; Longo, E.; Zhou, Y. A DFT Study of Structural and Electronic Properties of ZnS Polymorphs and its Pressure-Induced Phase Transitions. *J. Am. Ceram. Soc.* **2014**, *97*, 4011–4018.

(4) (a) Brafman, O.; Mitra, S. S. Raman Effect in Wurtzite- and Zinc-Blende-Type ZnS Single Crystals. *Phys. Rev.* **1968**, *171*, 931–934. (b) Wagner, H. P.; Kühnelt, M.; Langbein, W.; Hvam, J. M. Dispersion of the Second-Order Nonlinear Susceptibility in ZnTe, ZnSe, and ZnS. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *58*, 10494–10501. (c) Ding, Y.; Wang, X. D.; Wang, Z. L. Phase Controlled Synthesis of ZnS Nanobelts: Zinc Blende vs Wurtzite. *Chem. Phys. Lett.* **2004**, *398*, 32–36.

(5) (a) Shao, L. X.; Chang, K. H.; Hwang, H. L. Zinc Sulfide Thin Films Deposited by RF Reactive Sputtering for Photovoltaic Applications. *Appl. Surf. Sci.* **2003**, *212*, 305–310. (b) Subbaiah, Y. P. V.; Prathap, P.; Reddy, K. T. R. Structural, Electrical and Optical Properties of ZnS Films Deposited by Close-Spaced Evaporation. *Appl. Surf. Sci.* **2006**, *253*, 2409–2415. (c) Goudarzi, A.; Aval, G. M.; Sahraei, R.; Ahmadpoor, H. Ammonia-Free Chemical Bath Deposition of Nanocrystalline ZnS Thin Film Buffer Layer for Solar Cells. *Thin Solid Films* **2008**, *516*, 4953–4957.

(6) (a) Mandal, S. K.; Chaudhuri, S.; Pal, A. K. Optical Properties of Nanocrystalline ZnS Films Prepared by High Pressure Magnetron Sputtering. Thin Solid Films 1999, 350, 209-213. (b) Wei, M.; Choy, K. L. Deposition of Highly Oriented ZnS Thin Films on Si(100) Substrate Using Electrostatic Spray Assisted Vapor Deposition. Chem. Vap. Deposition 2002, 8, 15-17. (c) Hernández-Fenollosa, M. A.; López, M. C.; Donderis, V.; González, M.; Marí, B.; Ramos-Barrado, J. R. Role of Precursors on Morphology and Optical Properties of ZnS Thin Films Prepared by Chemical Spray Pyrolysis. Thin Solid Films 2008, 516, 1622-1625. (d) Chelvanathan, P.; Yusoff, Y.; Haque, F.; Akhtaruzzaman, M.; Alam, M. M.; Alothman, Z. A.; Rashid, M. J.; Sopian, K.; Amin, N. Growth and Characterization of RF-Sputtered ZnS Thin Film Deposited at Various Substrate Temperatures for Photovoltaic Application. Appl. Surf. Sci. 2015, 334, 138-144. (e) Le Donne, A.; Cavalcoli, D.; Mereu, R. A.; Perani, M.; Pagani, L.; Acciarri, M.; Binetti, S. Study of the Physical Properties of ZnS Thin

Films Deposited by RF Sputtering. *Mater. Sci. Semicond. Process.* 2017, 71, 7–11.

(7) (a) Frigo, D. M.; Khan, O. F. Z.; O'Brien, P. Growth of Epitaxial and Highly Oriented Thin Films of Cadmium and Cadmium Zinc Sulfide by Low-Pressure Metalorganic Chemical Vapour Deposition Using Diethyldithiocarbamates. J. Cryst. Growth 1989, 96, 989-992. (b) Hursthouse, M. B.; Malik, M. A.; Motevalli, M.; O'Brien, P. Mixed Alkyl Dialkylthiocarbamates of Zinc and Cadmium: Potential Precursors for II/VI Materials. X-ray Crystal Structure of [MeZnS₂CNEt₂]₂. Organometallics **1991**, 10, 730-732. (c) Seo, K. W.; Yoon, S. H.; Lee, S. S.; Shim, I. W. Preparation of ZnS Thin Film Using Zn(dithiocarbamate)₂ Precursors by MOCVD Method. Bull. Korean Chem. Soc. 2005, 26, 1582-1584. (d) Nyamen, L. D.; Nejo, A. A.; Pullabhotla, V. S. R.; Ndifon, P. T.; Malik, M. A.; Akhtar, J.; O'Brien, P.; Revaprasadu, N. The Syntheses and Structures of Zn(II) Heterocyclic Piperidine and Tetrahydroquinoline Dithiocarbamates and Their use as Single Source Precursors for ZnS Nanoparticles. Polyhedron 2014, 67, 129-135.

(8) (a) Barreca, D.; Tondello, E.; Lydon, D.; Spalding, T. R.; Fabrizio, M. Single-Source Chemical Vapor Deposition of Zinc Sulfide-Based Thin Films from Zinc bis(O-ethylxanthate). *Chem. Vap. Deposition* 2003, 9, 93–98. (b) Barreca, D.; Gasparotto, A.; Maragno, C.; Tondello, E.; Sada, C. CVD of Nanophasic (Zn, Cd)S Thin Films: From Multi-Layers to Solid Solutions. *Chem. Vap. Deposition* 2004, *10*, 229–236. (c) Barreca, D.; Gasparotto, A.; Maragno, C.; Seraglia, R.; Tondello, E.; Venzo, A.; Krishnan, V.; Bertagnolli, H. Synthesis and Characterization of Zinc Bis(O-isopropylxanthate) as a Single-Source Chemical Vapor Deposition Precursor for ZnS. *Appl. Organomet. Chem.* 2005, *19*, 1002–1009.

(9) Pawar, A. S.; Mlowe, S.; Garje, S. S.; Akerman, M. P.; Revaprasadu, N. Zinc Thiosemicarbazone Complexes: Single Source Precursors for Alkylamine Capped ZnS Nanoparticles. *Inorg. Chim. Acta* **2017**, *463*, 7–13.

(10) (a) Nyman, M.; Hampden-Smith, M. J.; Duesler, E. N. Low Temperature, Aerosol-Assisted Chemical Vapor Deposition (AACVD) of CdS, ZnS, and $Cd_{1-x}Zn_xS$ Using Monomeric Single-Source Precursors: M(SOCCH₃)₂TMEDA. *Chem. Vap. Deposition* **1996**, 2, 171–174. (b) Vittal, J. J.; Ng, M. T. Chemistry of Metal Thio- and Selenocarboxylates: Precursors for Metal Sulfide/Selenide Materials, Thin Films, and Nanocrystals. *Acc. Chem. Res.* **2006**, *39*, 869–877. (c) Vallejo-Sánchez, D.; Beobide, G.; Castillo, O.; Lanchas, M. Zinc Thiocarboxylate Complexes as Precursors for Zinc Sulfide Nanoparticles under Aerobic Conditions. *Eur. J. Inorg. Chem.* **2013**, *32*, 5592–5602.

(11) Byrom, C.; Malik, M. A.; O'Brien, P.; White, A. J. P.; Williams, D. J. Synthesis and X-ray Single Crystal Structures of Bis-(diisobutyldithiophosphinato)Cadmium(II) or Zinc(II): Potential Single-Source Precursors for II/VI Materials. *Polyhedron* **2000**, *19*, 211–215.

(12) Rojas-Montoya, I. D.; Santana-Silva, A.; García-Montalvo, V.; Muñoz-Hernández, M.-Á.; Rivera, M. N-(Chalcogen)phosphorylated (Chalcogen)ureas of Zinc and Cadmium(ii): SSPs for Group 12–16 Thin Films. *New J. Chem.* **2014**, *38*, 4702–4710.

(13) (a) Ramasamy, K.; Malik, M. A.; O'Brien, P.; Raftery, J. Metal Complexes of Thiobiurets and Dithiobiurets: Novel Single Source Precursors for Metal Sulfide Thin Film Nanostructures. *Dalton Trans.* **2010**, *39*, 1460–1463. (b) Ramasamy, K.; Malik, M. A.; Helliwell, M.; Raftery, J.; O'Brien, P. Thio- and Dithio-Biuret Precursors for Zinc Sulfide, Cadmium Sulfide, and Zinc Cadmium Sulfide Thin Films. *Chem. Mater.* **2011**, *23*, 1471–1481. (c) Abdelhady, A. L.; Malik, M. A.; O'Brien, P. Colloidal Synthesis of ZnS, CdS and Zn x Cd1–x S Nanoparticles from Zinc and Cadmium Thiobiuret Complexes. *J. Inorg. Organomet. Polym. Mater.* **2014**, *24*, 226–240.

(14) (a) Maury, F. Trends in Precursor Selection for MOCVD. *Chem. Vap. Deposition* **1996**, *2*, 113–116. (b) Afzaal, M.; Malik, M. A.; O'Brien, P. Chemical Routes to Chalcogenide Materials as Thin Films or Particles with Critical Dimensions with the Order of Nanometres. *J. Mater. Chem.* **2010**, *20*, 4031–4040.

(15) Gleizes, A. N. MOCVD of Chalcogenides, Pnictides, and Heterometallic Compounds from Single-Source Molecule Precursors. *Chem. Vap. Deposition* **2000**, *6*, 155–173.

(16) Marchand, P.; Hassan, I. A.; Parkin, I. P.; Carmalt, C. J. Aerosol-Assisted Delivery of Precursors for Chemical Vapour Deposition: Expanding the Scope of CVD for Materials Fabrication. *Dalton Trans.* **2013**, *42*, 9406–9422.

(17) (a) Pike, R. D.; Cui, H.; Kershaw, R.; Dwight, K.; Wold, A.; Blanton, T. N.; Wernberg, A. A.; Gysling, H. J. Preparation of Zinc Sulfide Thin Films by Ultrasonic Spray Pyrolysis from Bis-(diethyldithiocarbamato) Zinc(II). *Thin Solid Films* **1993**, 224, 221–226. (b) Nomura, R.; Murai, T.; Toyosaki, T.; Matsuda, H. Single-Source MOVPE Growth of Zinc Sulfide Thin Films using Zinc Dithiocarbamate Complexes. *Thin Solid Films* **1995**, 271, 4–7.

(18) Knapp, C. E.; Carmalt, C. J. Solution Based CVD of Main Group Materials. *Chem. Soc. Rev.* 2016, 45, 1036–1064.

(19) Buckingham, M. A.; Catherall, A. L.; Hill, M. S.; Johnson, A. L.; Parish, J. D. Aerosol-Assisted Chemical Vapor Deposition of CdS from Xanthate Single Source Precursors. *Cryst. Growth Des.* **2017**, *17*, 907–912.

(20) Powell, M. J.; Carmalt, C. J. Aerosols: A Sustainable Route to Functional Materials. *Chem. - Eur. J.* **2017**, *23*, 15543–15552.

(21) Catherall, A. L.; Harris, S.; Hill, M. S.; Johnson, A. L.; Mahon, M. F. Deposition of SnS Thin Films from Sn(II) Thioamidate Precursors. *Cryst. Growth Des.* **2017**, *17*, 5544–5551.

(22) Ahmet, I. Y.; Hill, M. S.; Johnson, A. L.; Peter, L. M. Polymorph-Selective Deposition of High Purity SnS Thin Films from a Single Source Precursor. *Chem. Mater.* **2015**, *27*, 7680–7688.

(23) Schmidt, S.; Schulz, S.; Bolte, M. $[^{t}BuC(N^{i}Pr)_{2}]_{2}Zn$ as Starting Reagent for Monoamidinate Zinc Complexes { $[^{t}BuC(N^{i}Pr)_{2}]ZnX$ }₂. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2210–2213.

(24) Wildsmith, T.; Hill, M. S.; Johnson, A. L.; Kingsley, A. J.; Molloy, K. C. Exclusive Formation of SnO by Low Temperature Single-Source AACVD. *Chem. Commun.*, **2013**, *49*, 8773

(25) (a) Kanters, J. A.; Spek, A. L.; Postma, R.; van Stein, G. C.; van Koten, G. Structure of Bis[N-(2-pyrrolylmethylene)-tert-butylamine]-Zinc(II), Zn $(C_9H_{13}N_2)_2$. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1983, 39, 999–1001. (b) Fernández-Galán, R.; Antiñolo, A.; Carrillo-Hermosilla, F.; López-Solera, I.; Otero, A.; Serrano-Laguna, A.; Villaseñor, E. Migratory Insertion Reactions in Asymmetrical Guanidinate-Supported Zirconium Complexes. Organometallics 2012, 31, 8360–8369.

(26) Johnson, A. L.; Hollingsworth, N.; Kociok-Köhn, G.; Molloy, K. C. Organozinc Aminoalcoholates: Synthesis, Structure, and Materials Chemistry. *Inorg. Chem.* **2008**, *47*, 12040–12048.

(27) Coles, M. P.; Hitchcock, P. B. Zinc Guanidinate Complexes and Their Application in Ring-Opening Polymerisation Catalysis. *Eur. J. Inorg. Chem.* **2004**, *13*, 2662–2672.

(28) (a) Benson, R. E.; Ellis, C. A.; Lewis, C. E.; Tiekink, E. R. T. 3D-, 2D- and 1D-Supramolecular Structures of {Zn[S2CN- $(CH_2CH_2OH)R]_2$ and their $\{Zn[S_2CN(CH_2CH_2OH)R]_2\}_2(4,4'$ bipyridine) Adducts for $R = CH_2CH_2OH$. Me or Et: Polymorphism and Pseudo-Polymorphism. CrystEngComm 2007, 9, 930-940. (b) Malik, M. A.; O'Brien, P. Mixed Methyl-Zinc and Ethylzinc Complexes with Diethylselenocarbamate - Novel Precursors for ZnSe. Chem. Mater. 1991, 3, 999-1000. (c) Memon, A. A.; Afzaal, M.; Malik, M. A.; Nguyen, C. Q.; O'Brien, P.; Raftery, J. The Nalkyldithiocarbamato Complexes $[M(S_2CNHR)_2]$ (M = Cd(II) Zn(II); R = C₂H₅C₄H₉C₆H₁₃C₁₂H₂₅); Their synthesis, thermal Decomposition and use to Prepare of Nanoparticles and Nanorods of CdS. Dalton Trans. 2006, No. 37, 4499-4505. (d) O'Brien, P.; Walsh, J. R.; Watson, I. M.; Motevalli, M.; Henriksen, L. Novel Dithio- and Diseleno-Carbamates of Zinc and Cadmium as Single-Molecule Precursors for Low-Pressure Metal-Organic Chemical Vapour Deposition. J. Chem. Soc., Dalton Trans. 1996, 12, 2491-2496.

(29) Drdácký, M.; Lesák, J.; Rescic, S.; Slížková, Z.; Tiano, P.; Valach, J. Standardization of Peeling Tests for Assessing the Cohesion and Consolidation Characteristics of Historic Stone Surfaces. *Mater. Struct.* **2012**, *45*, 505–520.

(30) Kole, A. K.; Kumbhakar, P. Cubic-to-Hexagonal Phase Transition and Optical Properties of Chemically Synthesized ZnS Nanocrystals. *Results Phys.* **2012**, *2*, 150–155.

(31) (a) Xiong, Q. H.; Wang, J. G.; Reese, O.; Voon, L.; Eklund, P. C. Raman Scattering from Surface Phonons in Rectangular Cross-Sectional W-ZnS Nanowires. *Nano Lett.* **2004**, *4*, 1991–1996. (b) Nilsen, W. G. Raman Spectrum of Cubic ZnS. *Phys. Rev.* **1969**, *182*, 838–850. (c) Kim, J. H.; Rho, H.; Kim, J.; Choi, Y. J.; Park, J. G. Raman Spectroscopy of ZnS Nanostructures. *J. Raman Spectrosc.* **2012**, *43*, 906–910. (d) Cheng, Y. C.; Jin, C. Q.; Gao, F.; Wu, X. L.; Zhong, W.; Li, S. H.; Chu, P. K. Raman Scattering Study of Zinc Blende and Wurtzite ZnS. *J. Appl. Phys.* **2009**, *106*, 123505-1–123505-5.

(32) Vallejos, S.; Umek, P.; Blackman, C. Aerosol Assisted Chemical Vapour Deposition Control Parameters for Selective Deposition of Tungsten Oxide Nanostructures. *J. Nanosci. Nanotechnol.* **2011**, *11*, 8214–8220.

(33) Vallejos, S.; Selina, S.; Annanouch, F. E.; Gràcia, I.; Llobet, E.; Blackman, C. Aerosol Assisted Chemical Vapour Deposition of Gas sensitive SnO_2 and Au-Functionalised SnO_2 Nanorods via a Non-Catalysed Vapour Solid (VS) Mechanism. *Sci. Rep.* **2016**, *6*, 1–12.

(34) (a) Madugu, M. L.; Olusola, O. I.-O.; Echendu, O. K.; Kadem, B.; Dharmadasa, I. M. Intrinsic Doping in Electrodeposited ZnS Thin Films for Application in Large-Area Optoelectronic Devices. *J. Electron. Mater.* **2016**, *45*, 2710–2717. (b) Yoo, D.; Choi, M. S.; Heo, S. C.; Chung, C.; Kim, D.; Choi, C. Structural, Optical and Chemical Analysis of Zinc Sulfide Thin Film Deposited by RF-Mganetron Sputtering and Post Deposition Annealing. *Met. Mater. Int.* **2013**, *19*, 1309–1316.

(35) (a) Yoon, Y. G.; Choi, I. H. Preparation of ZnS Thin Films by Using Photoassisted MOCVD. J. Korean Phys. Soc. 2013, 63, 1609-1614. (b) Xu, H.; Li, Y.; Rosa, A. L.; Frauenheim, T.; Zhang, R. Q. First-Principles Study of the Structural Stability and Electronic Properties of ZnS Nanowires. J. Phys. Chem. C 2008, 112, 20291-20294. (c) Wei, A. X.; Liu, J.; Zhuang, M. X.; Zhao, Y. Preparation and Characterization of ZnS Thin Films Prepared by Chemical Bath Deposition. Mater. Sci. Semicond. Process. 2013, 16, 1478-1484. (d) Schrier, J.; Demchenko, D. O.; Wang, L. W. Optical properties of ZnO/ZnS and ZnO/ZnTe Heterostructures for Photovoltaic Applications. Nano Lett. 2007, 7, 2377-2382. (e) Li, Z. Q.; Shi, J. H.; Liu, Q. Q.; Wang, Z. A.; Sun, Z.; Huang, S. M. Effect of Zn/S Ratios on the Properties of Chemical Bath Deposited Zinc Sulfide Thin Films. Appl. Surf. Sci. 2010, 257, 122-126. (f) Fang, X. S.; Zhai, T. Y.; Gautam, U. K.; Li, L.; Wu, L. M.; Yoshio, B.; Golberg, D. ZnS Nanostructures: From Synthesis to Applications. Prog. Mater. Sci. 2011, 56, 175-287.

(36) Rivillo, D.; Gulyás, H.; Benet-Buchholz, J.; Escudero-Adán, E. C.; Freixa, Z.; van Leeuwen, P.W. N. M. Catalysis by Design: Wide-Bite-Angle Diphosphines by Assembly of Ditopic Ligands for Selective Rhodium-Catalyzed Hydroformylation. *Angew. Chem., Int. Ed.* **2007**, *46*, 7247–7250.