Donor Solvent Mediated Reactions of Elemental Zinc and Sulfur, *sans* Explosion

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The reactions of zinc powder with solutions of elemental sulfur in various donor solvents is described. Complexes of the type \( \text{ZnS}_6(\text{N-donor})_2 \) are obtained for the ligands tetramethylethylenediamine (TMEDA), N-methylimidazole (MeIm), and 4-(N,N-dimethylamino)pyridine (DMAP). Ligand competition studies on pyridine solutions revealed that the relative stability constants (DMAP > MeIm > TMEDA > pyridine) parallel the basicity of the ligands. The TMEDA complex crystallizes in the monoclinic space group \( \text{C}2/c \) with \( a = 12.255(3) \, \text{Å}, \, b = 10.559(2) \, \text{Å}, \, c = 12.392(2) \, \text{Å}, \) and \( \beta = 110.22(2)^\circ \). In the solid state \( \text{ZnS}_6(\text{TMEDA}) \) adopts a tetrahedral geometry with a seven-membered \( \text{ZnS}_6 \) ring. A variety of reactivity studies were conducted on \( \text{ZnS}_6(\text{TMEDA}) \). Solutions of \( \text{ZnS}_6(\text{TMEDA}) \) undergo ligand exchange with quinuclidine and MeIm to afford \( \text{ZnS}_6(\text{L}_2) \) (\( L \equiv \text{MeIm}, \text{quinuclidine} \)). The anionic species \( [\text{ZnS}_{12}]^{2-} \) is formed upon addition of (PPh$_4$)$_2$S to \( \text{ZnS}_6(\text{TMEDA}) \). Optical and reactivity studies showed that MeIm, but not pyridine, displaces the polysulfide from \( \text{ZnS}_6(\text{MeIm})_2 \) as indicated by the appearance of the chromophore \( S_2^- \). \( \text{ZnS}_6(\text{TMEDA}) \) reacts with the electrophilic acetylenes dimethyl acetylenedicarboxylate and methyl propiolate to give the dithiolene complexes \( \text{ZnS}_2\text{C}_2\text{R}(\text{CO}_2\text{Me})(\text{TMEDA}) \) (\( R \equiv \text{CO}_2\text{Me}, \text{H} \)). Solid \( \text{ZnS}_6(\text{TMEDA}) \) cleanly decomposes at 350 °C as indicated by TGA studies. Preparative scale conversions at 500 °C affords cubic \( \text{ZnS} \). Submicron cubic \( \text{ZnS} \) is generated upon partial desulfurization of \( \text{ZnS}_6(\text{TMEDA}) \) with tertiary phosphines as established by electron microscopic studies.

Introduction

In a series of papers published during 1929-31, Coustal reported the preparation of \( \text{ZnS} \) using "la methode par explosion". This method entails igniting an intimate mixture of zinc and sulfur powder to give highly pure \( \text{ZnS} \) (eq 1). This reaction

\[
\text{Zn} + \frac{1}{2}\text{S}_\text{8} \rightarrow \text{ZnS} \quad \Delta H^\circ = -205.8 \, \text{kJ/mol} \quad (1)
\]

has been popularized in elementary textbooks and has been widely employed as a propellant in small rockets. We became interested in this process when we found that donor solvents promote the direct reaction of metal powders and sulfur. In contrast to Coustal's method, ours is not explosive; the donor solvent promotes the reaction without the need for an initiator (detonator), and the solvent absorbs excess heat. Furthermore the donor solvent binds to and stabilizes metal polysulfide intermediates. In this way the \( \text{L}-\text{Zn-S}_\text{8} (\text{L} \equiv \text{donor solvent}) \) route provides new zinc polysulfide complexes, some of which are promising sulfur transfer reagents. Our initial study on the \( \text{Zn} + \text{S}_\text{8} \) reaction employed \( \text{N}-\text{alkylimidazoles} \) as the donor solvents. The poor solubility of \( \text{ZnS}_6(\text{N-donor})_2 \) complexes limited exploration of their chemical properties. This report summarizes our successful efforts to address this limitation. The broader range of complexes uncovered has allowed us to expand the scope of our investigation to include reactivity of the resulting complexes.

Our interests in the \( \text{L}-\text{Zn-S}_\text{8} \) reaction are enhanced by the importance of \( \text{ZnS} \). This naturally occurring material is of importance in chemistry; for example: Metcalf, H. C.; Williams, J. E.; Castka, J. F. Modern Chemistry; Holt, Rinehart, Winston: New York, 1968; p 54. Aylett, B. J. Comprehensive Coordination Chemistry; Wilkinson, G., McCleverty, J., Gillard, R. D., Eds.; Pergamon: Oxford, U.K., 1984.

Results and Discussion

Solvent Mediated Reaction of \( \text{Zn} + \text{S}_\text{8} \). The synthetic method of interest involves dissolution of zinc powder in amine solutions of sulfur at mildly elevated temperatures. A variety of ligands such as \( \text{Zn(SMe)}_2 \) are promising sulfur transfer reagents. Our results on the \( \text{Zn} + \text{S}_\text{8} \) reaction are enhanced by the importance of \( \text{ZnS} \). This naturally occurring material is of importance in chemistry; for example: Metcalf, H. C.; Williams, J. E.; Castka, J. F. Modern Chemistry; Holt, Rinehart, Winston: New York, 1968; p 54. Aylett, B. J. Comprehensive Coordination Chemistry; Wilkinson, G., McCleverty, J., Gillard, R. D., Eds.; Pergamon: Oxford, U.K., 1984.
Table 1. Donor Ligands Examined for Preparation of ZnS₆(donor)₂ Complexes

<table>
<thead>
<tr>
<th>ligands</th>
<th>pKₐ</th>
<th>synthesis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylimidazole (MeIm)</td>
<td>7.3±b</td>
<td>neat/90 °C/12 h</td>
</tr>
<tr>
<td>pyridine (py)</td>
<td>5.2±c</td>
<td>neat/115 °C/48 h</td>
</tr>
<tr>
<td>tetramethylenediamine (TMEDA)</td>
<td>5.8±,8.9±d</td>
<td>neat/90 °C/2 h</td>
</tr>
<tr>
<td>dimethylaminopyridine (DMAP)</td>
<td>9.7±</td>
<td>DMF soln/90 °C/10 h</td>
</tr>
<tr>
<td>quinuclidine</td>
<td>10.0±f</td>
<td>ligand exchange from ZnS₆(TMEDA)</td>
</tr>
</tbody>
</table>


Figure 1. IR spectra of various polysulfide complexes in the region associated with υS=O: ZnS₆(MeIm)₂ (a), ZnS₆(TMEDA) (b), ZnS₆(DMAP) (c), (PPP₄)₂[ZnS₆] (d).

of amines were tested (Table 1). Our benchmark reaction involves treatment of zinc dust with an N-methylimidazole-(MeIm) solution of sulfur (eq 2). One observes the dissolution

$$Zn + \frac{5}{6}S₈ + 2L \rightarrow ZnS₆(L)₂$$

L = MeIm, Me₂NC₃H₄N, py, 0.5TMEDA

of the zinc over the course of a few hours at 90 °C. Dilution of the cooled reaction mixture with a nonpolar solvent, such as toluene, leads to precipitation of yellow microcrystals of ZnS₆-(MeIm)₂.  

The Zn + S₈ reaction is also promoted by 4-(N,N-dimethylamino)pyridine (DMAP). In this case the synthesis requires only stoichiometric amounts of the reactants in hot DMF. The resulting ZnS₆(DMAP)₂ is an air and water stable yellow microcrystalline species. Its ¹H NMR spectrum is virtually unshifted vs the free ligand.  

Its IR spectrum in the 600-400 cm⁻¹ range closely resembles that for the structurally characterized ZnS₆(TMEDA) except for a ligand band at 525 cm⁻¹ (Figure 1). ZnS₆(DMAP)₂ is a nonelectrolyte in DMF solution.

The complex ZnS₆(py)₂ has recently been reported to form from the py-Zn-S₈ reaction. We briefly checked these results since few preparative details were provided.  

We were unable to detect any reaction between sulfur and zinc in pyridine. Subsequent studies showed that the reaction does proceed when technical grade pyridine is used. The impurities in the technical grade pyridine appear to activate the zinc, a factor which is especially important in this very sluggish reaction. Although the complex is poorly soluble, ZnS₆(py)₂ is still of some preparative interest since the pyridine ligands are very labile.

The versatile species ZnS₆(TMEDA) was synthesized by the direct reaction of the elements in neat TMEDA. This complex is soluble in a wide variety of solvents such as DMF, acetonitrile, THF, warm toluene, and even hot alkanes. We specifically verified that CH₂Cl₂ solutions of ZnS₆(TMEDA) were stable under N₂ since we suspected the possibility of S-alkylation affording species such as S₆CH₂. In contrast to the TMEDA complex, most other ZnS₆L₂ compounds are soluble only in very strong donor solvents such as pyridine, DMF, and MeIm. An added attraction to this TMEDA complex is the lability of the TMEDA. This complex is insoluble in and does not react with CS₂.

Other amines that were tested without success (no conversion of the Zn powder) include triethylamine and N,N-dimethylbenzylamine.

Structure of ZnS₆(TMEDA). A crystallographic study of ZnS₆(TMEDA) revealed zinc in a pseudotetrahedral ligand environment defined by its coordination to the nitrogen atoms of TMEDA and two sulfur atoms of the hexasulfido chelate (Figure 2). Crystallographic 2-fold symmetry was imposed. The bite angle of the TMEDA (86.81(6)°) is similar to that (86°) seen in Zn(NO₃)₂(TMEDA) which features O-bound nitrito


ligands. The bite angle of the polysulfide chelate is 119.73-2°. The metrical details of the $\text{ZnS}_6$ ring are similar to those in $\text{ZnS}_6$(MeIm)$_2$ while the Zn–S distances resemble those seen in zinc thiocyanates. An interesting feature is that the ring conformation of $\text{S}_7$ and the $\text{ZnS}_6$ rings adopt similar conformations but differ in one important respect. In cyclo-$S_7$, one finds a very long S–S distance of 2.18 Å for the central two sulfur atoms associated with the planar $\text{S}_5$ array. This long distance has been attributed to a repulsive interaction between the sulfur atoms associated with the 0° dihedral angle. In $\text{ZnS}_6$(TMEDA) the Zn atom occupies one of the 0° dihedral sites, thus allowing the remainder of the polysulfide to adopt a conventional geometry.

Polysulfide Displacement Reactions. Pyridine solutions of the polysulfide complexes appear yellow; optical measurements confirm the absence of absorptions in the 500–800 nm region. These data are typical for classical zinc complexes of anionic sulfur ligands, e.g., $\text{Zn}(\text{S}^-\text{P}^-\text{S})\text{MeIm}_2$. In contrast, MeIm solutions of $\text{ZnS}_6\text{(MeIm)}_2$ and $\text{ZnS}_6$(TMEDA) are intensely greenish-blue with an absorption maximum at 614 nm. This low-energy band is assigned to the trisulfide radical anion $\text{S}_7^-$ and has been observed previously in solutions of polysulfide anions (eqs 3 and 4). Support for this assignment comes from

$$\text{ZnS}_6(\text{TMEDA}) + 6\text{MeIm} \rightleftharpoons \text{Zn(MeIm)}_6^{2+} + \text{S}_7^- \quad (3)$$

the observation of the same absorption maximum for MeIm solutions of (PPPh)$_3\text{S}_6$. The fact that pyridine solutions of these zinc complexes do not contain the trisulfide anion is a consequence of the inability of pyridine to displace the elements of $\text{S}_7^-$ from the coordination sphere of zinc. Using (PPh)$_3\text{S}_6$, we confirmed that in pyridine solutions $\text{S}_7^-$ dissociates into $\text{S}_7^-$. The non-dissociation of $\text{S}_7^-$ from $\text{ZnS}_6\text{L}_2$ by pyridine is consistent with the lower basicity of py relative to MeIm. Even more important we think is the fact that pyridine is bulkier than MeIm and has been observed previously in solutions of polysulfide anions (eqs 3 and 4).

The ability of MeIm to displace the polysulfide ligand is relevant to the oxygen sensitivity of MeIm solution of $\text{ZnS}_6\text{(MeIm)}_2$. Prolonged exposure of MeIm solutions of $\text{ZnS}_6\text{(MeIm)}_2$ to air converts the polysulfide complex into the orange-yellow crystals of $\text{ZnS}_6\text{O}_3\text{(MeIm)}_3$. This water soluble zwitterionic species shows a $\nu_{\text{S=O}}$ at 1163 cm$^{-1}$, typical of an S-bound thiosulfate. The structure of $\text{ZnS}_6\text{O}_3\text{(MeIm)}_3$ was confirmed by single crystal X-ray diffraction. The oxidation of aqueous sulfide solution is known to give thiosulfate.$^{21}$

Ligand Exchange Studies. Insights into the relative stability of the amine adducts were provided by $^1\text{H NMR}$ studies on pyridine-$d_5$ solutions of the zinc polysulfides. These experiments were possible in part because of the aforementioned results showing that the polysulfide ligand is not displaced from the zinc by neat pyridine. The $^1\text{H NMR}$ spectrum of $\text{ZnS}_6\text{(MeIm)}_2$ is rather simple, consisting only of four resonances for the four types of MeIm protons. The observed chemical shifts are concentration dependent and do not correspond to the signals of free MeIm in pyridine, indicating the effects of coordination. The overall simplicity of the spectra are consistent with fast ligand exchange typical for divalent zinc complexes.$^{23}$ The signal for 2-H (the methylene hydrogen situated between the two nitrogen centers) proved most sensitive to changes in the concentration. The chemical shifts range from 7.70 ppm for 2.85 mM solutions to 8.03 ppm for 0.334 M solutions. The fact that the shift for the most dilute solution approaches that of free MeIm (7.65 ppm) indicates that both MeIm ligands are displaced from the zinc under these conditions. The equilibrium can be described as shown in eqs 5 and 6.

$$\text{ZnS}_6(\text{MeIm})_2 + 2\text{py} \rightleftharpoons \text{ZnS}_6(\text{py})_2 + 2\text{MeIm} \quad (5)$$

chemical shift data, we estimated (see Experimental Section) that the equilibrium constant for the displacement of both MeIm ligands by pyridine is $\sim 9 \times 10^{-5}$. In view of this small equilibrium constant it is understandable that attempts to prepare $\text{ZnS}_6\text{(py)}_2$ via ligand exchange from $\text{ZnS}_6\text{(MeIm)}_2$ would be unsuccessful, as was established by the fact that $\text{ZnS}_6\text{(MeIm)}_2$ can be recrystallized from pyridine solution.

$^1\text{H NMR}$ studies revealed that (dimethylamino)pyridine (DMAP) completely displaced MeIm from $\text{ZnS}_6(\text{MeIm})_2$ in pyridine-$d_5$ solution. The chemical shifts for TMEDA are insensitive to the effects of coordination, while preparative experiments demonstrated that TMEDA is a poorer donor toward $\text{ZnS}_6$ than MeIm but better than py. The trend in binding efficiencies is thus

$$\text{DMAP} > \text{MeIm} > \text{TMEDA} > \text{py}$$

which correlates with the basicity of the nitrogen donor ligand (Table 1).$^{21}$ $^1\text{H NMR}$ studies showed that quinuclidine also displaces TMEDA from $\text{ZnS}_6$(TMEDA) giving $\text{ZnS}_6$ (quinuclidine).$^{24}$ In addition to undergoing exchange with neutral donor ligands, $\text{ZnS}_6$(TMEDA) reacts with $\text{S}_7^-$ to give the known $\text{ZnS}_6(\text{S}_7^-)$.$^{25}$

Acetylene Addition Reactions. Polysulfide complexes characteristically react with electrophilic acetylenes such as ester- and trifluoromethyl-substituted acetylenes.$^{26,27}$ The dim-

(19) Vaid, T.; Rauchfuss, T. B.; Krautkheis, H. Unpublished results. $\text{C}_6\text{H}_4\text{NO}_3\text{S}_2\text{Zn}$ crystallizes in the orthorhombic space group $\text{P}2_1\text{a}$, $a = 9.330(4) \text{Å}$, $b = 13.393(6) \text{Å}$, $c = 14.416(3) \text{Å}$, and $\alpha = \beta = \gamma = 90°$. Unit cell volume is $1797.3 \text{Å}^3$, and $Z = 4$. Mo Kα radiation was used. $R_\text{wp} = 0.1305$. The scan range (2θ, deg) 2–52. Measured reflections = 2428, and unique reflections = 1870. $R_\text{wp} = 2.91\%$, $R = 5.63$, and $R_\text{wp} = 5.86\%$.
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Figure 3. Thermogravimetric analysis of ZnS₆(TMEDA) under flowing He with a heating rate of 10 °C/min.

ethyl ester of acetylenedicarboxylic acid reacted readily with ZnS₆(TMEDA) to yield the dithiolene complex ZnS₂C₂(CO₂Me)(TMEDA). The light yellow microcrystalline solid shows three resonances in its ¹H NMR spectrum, indicative of a very simple structure. The IR spectrum is featureless in the νss region; absorptions at 1720 and 1685 cm⁻¹ are assigned to the νco and νC≡C vibrations, respectively. The less electrophilic acetylene methyl propiolate behaved similarly, although this reaction required elevated temperatures. We obtained good yields of bright yellow microcrystalline solid analyzing as ZnS₂C₂H(CO₂Me)(TMEDA). We observed no reaction between ZnS₆(TMEDA) and diphenylacetylene, dimethylfumarate, or norbornene.

The ¹H NMR spectrum of ZnS₂C₂H(CO₂Me)(TMEDA) features two peaks in the N(CH₃)₂ region. On the basis of a tetrahedral structure, one might expect that there would be two sets of nonequivalent N-methyl groups. The 400 MHz ¹H NMR spectrum of this species remains essentially unchanged at −35 °C. The N–Me sites could be equivalenced either via tetrahedral–square planar interconversion or an associative process.

Conversion of Zinc Polysulfides to ZnS. The conversion of the zinc polysulfide complexes to zinc sulfide was effected both thermally and chemically. Particular emphasis was placed on ZnS₆(TMEDA) since this species is so easily prepared and is soluble in nonpolar solvents. Thermogravimetric analysis (TGA) of this complex revealed decomposition events centered at 180 and 260 °C. On the basis of weight changes, these processes correspond to the loss of TMEDA followed by five sulfur atoms, respectively (Figure 3). The loss of sulfur atoms occurs over an 80 °C temperature range, and the process observed is identical to that seen for elemental sulfur. The net weight yield is ~26% (theory: 26.06%). The TGA of ZnS₅(DMAP)₂ shows the same pattern. The thermolysis of ZnS₆(TMEDA) was also carried out on a preparative scale at 500 °C under flowing nitrogen. The elemental composition of the light-gray colored residue corresponds to pure ZnS, and its powder X-ray diffraction indicated the cubic form of ZnS. The material obtained after pyrolysis at 500 °C does not dissolve in TMEDA solutions of sulfur.

It was found that THF solutions of ZnS₆(TMEDA) convert Pb₃ to SPb₃ as indicated by ³¹P NMR analysis of reaction solutions. When conducted on a preparative scale, treatment of ZnS₆(TMEDA) with 5 equiv of Pb₃ afforded colorless suspensions of ZnS which can be filtered only with difficulty. Electron microscopic examination of the resulting solid established an average particle size of approximate diameter of 0.11 μm (Figure 4). When substoichiometric amounts (< 5 equiv) of Pb₃ are employed we still observed the formation of ZnS, although in diminished yields. For example the reaction of ZnS₆(TMEDA) with 2 equiv Pb₃ gave a 33% yield (theory: 40%) of ZnS together with unreacted starting complex. These experiments suggest that complexes of the type ZnS₅(TMEDA) (x < 6) readily redistribute as described in pathway A of Scheme 1. An alternative, of several possible mechanisms, is presented as case B in the Scheme. This pathway implies that ZnS₅(TMEDA) is more reactive toward Pb₃ than the starting hexasulfide. Freshly prepared samples of this submicron ZnS proved unreactive toward a solution of elemental sulfur in TMEDA. Collectively these experiments suggest that ZnS₅(TMEDA) is thermodynamically unstable with respect to ZnS; hence, ZnS₆(TMEDA) is a kinetically stabilized intermediate in the reaction of Zn and S₈ in TMEDA.

Conclusions

In the first part of the work we have developed routes to zinc polysulfides which exploit the donor solvent assisted oxidation of zinc powders. We have previously referred to this synthesis method as L−M−X, where L is a donor ligand (as solvent or solute), M is a source of metal(0), and X is the oxidant. While such L−M−X reactions are common for X =

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Figure 4. Scanning electron micrograph of ZnS produced by reaction of ZnS₆(TMEDA) with PBu₃. The magnification is 20000× and 100000×, respectively.

Scheme 1

\[
\begin{align*}
\text{ZnS}_6(\text{TMEDA}) + \text{PBu}_3 &\rightarrow [\text{ZnS}_6(\text{TMEDA})] + \text{PBu}_3 \\
\text{ZnS}_6(\text{TMEDA}) + \text{S} &\rightarrow \text{ZnS} + \text{TMEDA}
\end{align*}
\]

halogen, the use of elemental sulfur as an oxidant is unusual. Within the context of the L-M-S₈ reaction, the present work is significant because it has identified several new donors (L). Furthermore, we have demonstrated that the efficiency of the L-Zn-S₈ reaction correlates with the Bronsted basicity of L. The very basic (dimethylamino)pyridine promotes the formation of a zinc polysulfide so effectively that the reactions can be conducted using stoichiometric amounts of the reagents in DMF. At the other extreme, the bpy-Zn-S₈ reaction is extremely sluggish. The stability of ZnSₓNₓ coordination is very robust as indicated by the widespread occurrence of the so-called zinc finger motif wherein zinc is coordinated to pairs of imidazoles and thiocarboxylates.

Strongly basic ligands displace the polysulfide ligand from ZnS₆L₂ as revealed by the formation of S₅₂⁻ which arises via the fragmentation of the displaced S₆²⁻ in polar solvents. The ability of MeIm, but not bpy, to displace the polysulfide parallels the results of the ligand competition studies and also reflects the added stability of complexes of the type Zn(MeIm)₆²⁺. A consequence of polysulfide displacement is that solutions of ZnSₓNₓ in strong donor solvents exhibit enhanced reactivity toward oxygen, evidenced by our isolation of a thiosulfato complex.

The most attractive complex for further studies is ZnS₆⁻(TMEDA). This species forms in very high yields and is air


(28) We investigated the possibility that DMAP would promote the formation of cadmium polysulfides; instead we observed the formation of CdS.


stable and soluble in a variety of organic solvents. In contrast, the majority of zinc polysulfides are prepared via less efficient procedures and they are ionic and hence soluble in a limited range of polar organic solvents. An important advantage to ZnS₆(TMEDA) is that the diamine can be readily displaced by a variety of other ligands. Application of ZnS₆(TMEDA) as a polysulfide transfer reagent is currently under study.

A final theme of this project concerns the role of metal polysulfides as mechanistic links between the chemistry of sulfur and binary metal sulfides (eq 7). The complexes ZnS₆L² represent donor-stabilized intermediates in the reaction of sulfur and zinc. The polysulfide complexes convert to ZnS upon heating. Another route to ZnS resulted from our attempts to contract the polysulfide chelate using the sulfur-abstracting agent PBu₃. This chemical method afforded submicron particles of ZnS. It is interesting that the desulfurization of ZnS₆(TMEDA) generates ZnS, even with substoichiometric amounts of PBu₃. These experiments suggest that ZnS formation occurs via aggregation of ZnS, species where x < 6. Further studies along these lines may identify new Zn-S clusters.

Experimental Section

All experimental manipulations were performed under a dinitrogen atmosphere using standard Schlenk-line techniques, unless mentioned otherwise. N-methylimidazole (99.9%, Aldrich) and dimethylformamide (Fisher) were distilled from BaO at reduced pressure (0.1 mmHg, 70–75 °C and 38–42 °C, respectively) and stored under nitrogen. Pyridine (Fisher) was dried over KOH for 24 h and then distilled over BaO at 115 °C. Dichloromethane was distilled over anhydrous CaH₂. Tetrahydrofuran, hexane, and diethyl ether were distilled over sodium/benzophenone. Zinc (-325 mesh, Cerac), sulfur (99.9%, E & M Science) were used as obtained: N,N,N'N'-Tetramethylhexanediimine (TMEDA), 4-(N,N-dimethylamino)pyridine (DMAP), dimethyl acetylenedicarboxylate (DMAD), and methyl propiolate were obtained from Aldrich and used as received. (PPh₃)₂S₈ was prepared by the addition

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Scheme 2

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Conditions: (i) 350 °C; (ii) C2(CO2Me)R (R = H, CO2Me); (iii) Me2NC6H4N; (iv) (PPh4)3S6; (v) Me2NCl2.

of a slurry of 1.57 g of PPh4Cl in 20 mL of H2O to a solution of 0.135 g of S8 and 0.51 g of Na2S·9H2O in 10 mL of H2O.

The following instruments were employed: Mattson Galaxy Series 3000 FTIR spectrometer, an HP 8452A diode array spectrophotometer (UV-vis), and a Rigaku D-Max powder X-ray diffractometer with a Cu target (X-ray diffraction). Solution NMR spectra were recorded with Varian NMR spectrometers operating at 200 MHz (XL200) or 400 MHz (U400). Microanalyses and thermogravimetric analyses (TGA) were performed by the School of Chemical Sciences Microanalytical Laboratory.

SEM images were recorded with a Hitachi S-800 high resolution scanning electron microscope with field emission electron source operating at 20 kV accelerating voltage. The sample was supported on a conductive carbon tape. The composition of the sample was checked by EDX. Transmission electron micrographs were recorded using a Phillips 400 instrument. The sample was deposited on a copper grid with carbon film. The d-spacings were calculated from the electron diffraction data and matched with those of the cubic phase of ZnS. ZnS6(MeIm)2.

A mixture of 3.53 g of zinc powder (54 mmol) and 10.43 g of sulfur (325 mmol) in 78 mL of dry MeIm was stirred in a Schlenk flask at 90 °C for 16 h. After cooling to room temperature, the dark red reaction mixture was diluted with 100 mL of Et2O and stored at -5 °C. After 6 h the resulting yellow powder was filtered out and washed with Et2O. The crude product was extracted into ~70 mL of MeIm which was diluted with ca. 100 mL of Et2O. Yield: 13.28; S, 45.58; Zn, 15.49. Found: C, 23.22; H, 2.93; N, 13.63. IR (KBr): 495 cm⁻¹ (VSS).

ZnS6(TMEDA). A Schlenk flask was charged with 2.61 g of zinc dust (39.9 mmol) and 10.43 g of sulfur (325 mmol) in 78 mL of dry MeIm was stirred in a Schlenk flask at 90 °C for 16 h. After cooling to room temperature, the dark red reaction mixture was diluted with 100 mL of Et2O and stored at -5 °C. After 6 h the resulting yellow powder was filtered out and washed with Et2O. The crude product was extracted into ~70 mL of MeIm which was diluted with ca. 100 mL of Et2O. Yield: 13.28; S, 45.58; Zn, 15.49. Found: C, 23.22; H, 2.93; N, 13.63. IR (KBr): 495 cm⁻¹ (VSS).

ZnS6(DMAP). A mixture of 0.655 g of zinc dust (10 mmol), 1.947 g of sulfur (60.7 mmol), and 1.303 g of DMAP (20.1 mmol) in 30 mL of DMF was stirred at 90 °C for 16 h. After cooling to room temperature, the yellowish reaction mixture was diluted with ca. 60 mL of Et2O. The resulting yellow solid was collected and washed with 3 × 20 mL portions of Et2O. The crude product was recrystallized from DMF and ether. Yield: 3.87 g (77%).

ZnSn(py). A mixture of 2.65 g of zinc (40.5 mmol) and 11.81 g of sulfur (368.4 mmol) in 78 mL of dry MeIm was stirred in a Schlenk flask at 90 °C for 16 h. After cooling to room temperature, the dark red reaction mixture was diluted with 100 mL of Et2O and stored at -5 °C. After 6 h the resulting yellow powder was filtered out and washed with Et2O. The crude product was extracted into ~70 mL of MeIm which was diluted with ca. 100 mL of Et2O. Yield: 13.28; S, 45.58; Zn, 15.49. Found: C, 23.22; H, 2.93; N, 13.63. IR (KBr): 495 cm⁻¹ (VSS).

ZnS6(quinuclidine). A Schlenk flask was charged with 0.298 g of ZnS6(TMEDA) (0.8 mmol), 0.417 g of quinuclidine (1.6 mmol), and 10 mL of dry pyridine. The reaction mixture was stirred at room temperature for 24 h. After cooling to room temperature, the yellowish reaction mixture was diluted with 100 mL of Et2O. The crude product was recrystallized from pyridine/Et2O and washed with Et2O followed by CS2. Yield: 8.37 g (50%).

ZnSn(py)2. A mixture of 2.65 g of zinc (40.5 mmol) and 11.81 g of sulfur (368.4 mmol) was refluxed in unpurified pyridine for ca. 70 h. After cooling to room temperature, the yellow suspension was diluted with 200 mL of Et2O. The crude product was filtered and recrystallized from pyridine/Et2O and washed with Et2O followed by CS2. Yield: 8.37 g (50%).

ZnSn(quinuclidine). A Schlenk flask was charged with 0.298 g of ZnS6(TMEDA) (0.8 mmol), 0.417 g of quinuclidine (1.6 mmol), and 10 mL of dry pyridine. The yellow solution was stirred for 24 h. After dilution with 100 mL of Et2O, the resulting yellow solid was filtered out, washed with Et2O, and dried under vacuum. Yield: 0.290 g (75%).

ZnSn(py)2. A mixture of 2.65 g of zinc (40.5 mmol) and 11.81 g of sulfur (368.4 mmol) was refluxed in unpurified pyridine for ca. 70 h. After cooling to room temperature, the yellow suspension was diluted with 200 mL of Et2O. The crude product was filtered and recrystallized from pyridine/Et2O and washed with Et2O followed by CS2. Yield: 8.37 g (50%).

ZnSn(quinuclidine). A Schlenk flask was charged with 0.298 g of ZnS6(TMEDA) (0.8 mmol), 0.417 g of quinuclidine (1.6 mmol), and 10 mL of dry pyridine. The yellow solution was stirred for 24 h. After dilution with 100 mL of Et2O, the resulting yellow solid was filtered out, washed with Et2O, and dried under vacuum. Yield: 0.290 g (75%).

The NMR spectrum of a sample in py-d5 solution showed ~1% of ZnSn(TMEDA). 1H NMR (pyridine-d5): δ 8.37 (d, 2H), 6.45 (d, 2H), 2.72 (s, 6H). IR (KBr): 494 cm⁻¹ (VSS).

(PPh4)2[ZnS12]. To a mixture of 0.331 g of ZnSn(TMEDA) (0.8 mmol) and 0.144 g of (PPh4)2As (0.8 mmol) in Schlenk flask was added 5 mL of MeCN with stirring. The initial brownish-red color immediately changed to yellow with appearance of yellow microcrystalline solid. After being stirred at room temperature for 6 h, the reaction mixture was diluted with 30 mL of Et2O. The yellow microcrystalline solid was washed with several portions of Et2O and...
dried under vacuum. Yield: 0.34 g (78%). Anal. Calcd for C_{6}H_{12}N_{2}O_{4}S_{2}Zn: C, 51.07; H, 3.57; N, 16.53; Zn, 16.86. Found: C, 50.83; H, 3.46; N, 16.53; Zn, 16.86.

ZnS_{2}C_{2}(CO\textsubscript{2}Me)(TMEDA). A solution of 0.226 g of ZnS_{2}C_{2}(CO\textsubscript{2}Me)(TMEDA) (0.6 mmol) in 6 mL of warm THF was treated with 1.5 mL of methyl propiolate (16.8 mmol), and the reaction mixture was stirred at room temperature for 9 h and then filtered. The orange-yellow residue was washed with small portions of cold THF and hexane to afford ZnS_{2}C_{2}(CO\textsubscript{2}Me)(TMEDA) as a light yellow colored solid. Yield: 0.107 g (46%). Anal. Calcd for C_{10}H_{20}N_{2}O_{2}S_{2}Zn: C, 36.42; H, 6.11; N, 7.8; S, 32.64; Zn, 5.18. Found: C, 36.28; H, 6.05; N, 7.8; S, 32.64; Zn, 5.18.

Thermal Decomposition of ZnS_{6}(TMEDA). A porcelain boat, charged with 0.506 g of diethyl acetylenedicarboxylate (1.8 mmol), was loaded into a tube-furnace. The temperature was first raised gradually to 500 °C and then increased to 600 °C where it was maintained for 26 h and then cooled to 25 °C. The yield was 0.131 g of white-gray residue. The 0.131 g of white-gray residue corresponds to 84% yield of the starting material (theoretical weight yield is 0.155 g). A solution of 1.381 g of ZnS_{6}(TMEDA) (3.7 mmol) in 25 mL of warm THF was treated with 5 mL of cold THF followed by 10 mL portions of hexane. Yield: 0.34 g (78%). Anal. Calcd for C_{10}H_{20}N_{2}O_{2}S_{2}Zn: C, 36.42; H, 6.11; N, 7.8; S, 32.64; Zn, 5.18. Found: C, 36.28; H, 6.05; N, 7.8; S, 32.64; Zn, 5.18.

X-ray Diffraction Study of ZnS_{6}(TMEDA). Suitable crystals for X-ray studies were obtained by layering a DMF solution of ZnS_{6}(TMEDA) with ether. The light yellow, transparent columnar crystal was cut from a larger crystal which had well-developed faces. There were no crystallites or other contaminating substances attached to the surface of the sample. The crystal was mounted using oil (Paratone, Exxon) to a thin glass fiber and then cooled to −75 °C with the (514) scattering planes roughly normal to the spindle axis. The data crystal was approximately bound by the {110}, {100}, {110}, and {001} inversion forms. Distances from the crystal center to these faces were determined by visual inspection, with 0.05, 0.07, 0.08, and 0.27 mm, respectively.

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Supplementary Material Available: Tables of thermal parameters and bond angles and distances (2 pages). Ordering information is given on any current masthead page.

Table 2. Crystallographic Parameters of ZnS_{6}(TMEDA)