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 ZnS_6(*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 *C*2/*c* with $a = 12.255(3)$ Å, $b = 10.559(2)$ Å, $c = 12.392(2)$ Å, and $\beta = 110.22(2)°$. In the solid state ZnS_6(TMEDA) adopts a tetrahedral geometry with a seven-membered ZnS_6 ring. A variety of reactivity studies were conducted on ZnS_6(TMEDA). Solutions of ZnS_6(TMEDA) undergo ligand exchange with quinuclidine and MeIm to afford ZnS_6L_2 (L = MeIm, quinuclidine). The anionic species $[ZnS_{12}]^{2-}$ is formed upon addition of $(PPh_4)_2S_6$ to ZnS_6(TMEDA). Optical and reactivity studies showed that MeIm, but not pyridine, displaces the polysulfide from $ZnS_6(MeIm)_2$ as indicated by the appearance of the chromophore S_3^-. ZnS_6(TMEDA) reacts with the electrophilic acetylenes dimethyl acetylenedicarboxylate and methyl propiolate to give the dithiolene complexes $ZnS_2C_2R(CO_2Me)$(TMEDA) {R = CO_2Me, H}. Solid ZnS_6(TMEDA) cleanly decomposes at 350 °C as indicated by TGA studies. Preparative scale conversions at 500 °C affords cubic ZnS. Submicron cubic ZnS is generated upon partial desulfurization of ZnS_6(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 ZnS using "la methode par explosion".[1] This method entails igniting an intimate mixture of zinc and sulfur powder to give highly pure ZnS (eq 1). This reaction

$$Zn + {}^1/_8S_8 \rightarrow ZnS\ (cubic) \qquad \Delta H° = -205.8\ kJ/mol \quad (1)$$

has been popularized in elementary textbooks[2] 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.[3] 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 polysulfido intermediates. In this way the L−Zn−S_8 (L = donor solvent) route provides new zinc polysulfide complexes, some of which are promising sulfur transfer reagents. Our initial study on the Zn + S_8 reaction employed *N*-alkylimidazoles as the donor solvents. The poor solubility of the $ZnS_6(RIm)_2$ 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 L−Zn−S_8 reaction are enhanced by the importance of ZnS. This naturally occurring material is produced industrially for a variety of applications,[4,5] especially as a pigment and a phosphor.[6] Common methods for synthesis include direct combination of sulfur and zinc, treatment of ZnO with H_2S,[7] and precipitation from aqueous solutions of Zn^{2+} with sources of S^{2-}.[2] More specialized routes to ZnS films involve the reaction of H_2S with $ZnEt_2$.[8] Alternatively, ZnS can be obtained by the thermal cracking of mercaptide complexes such as $Zn(SMe)_2$.[9] The new ZnS_6L_2 complexes reported in this paper readily convert to ZnS.

Results and Discussion

Solvent Mediated Reaction of Zn + S_8. The synthetic method of interest involves dissolution of zinc powder in amine solutions of sulfur at mildly elevated temperatures. A variety

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Table 1. Donor Ligands Examined for Preparation of $ZnS_6(donor)_2$ Complexes

ligands	pK_a	synthesis conditions
methylimidazole (MeIm)	7.3[a,b]	neat/90 °C/12 h
pyridine (py)	5.23[c]	neat/115 °C/48 h
tetramethylethylenediamine (TMEDA)	5.85, 8.97[d]	neat/90 °C/2 h
dimethylaminopyridine (DMAP)	9.7[e]	DMF soln/90 °C/10 h
quinuclidine	10.05[f]	ligand exchange from ZnS_6(TMEDA)

[a] Paiva, A. C. M.; Juliano, L.; Boschcov, P. *J. Am. Chem. Soc.* **1976**, *98*, 7645. [b] Sheinker, V. N.; Tishchenko, L. G.; Garnovskii, A. D.; Osipov, O. A. *Chem. Heterocycl. Comp. (Engl. Trans.)* **1975**, *11*, 504. [c] Albert, A. In *Physical Methods in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1971; Vols. 1 and 3, p 1. [d] Spialter, L.; Moshier, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 5955. [e] Ramsey, B. G.; Walker, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 3314. [f] Coll, J. C.; Crist, D. R.; Barrio, M. C. G.; Leonard, N. J. J. Am. Chem. Soc. **1972**, *94*, 7092.

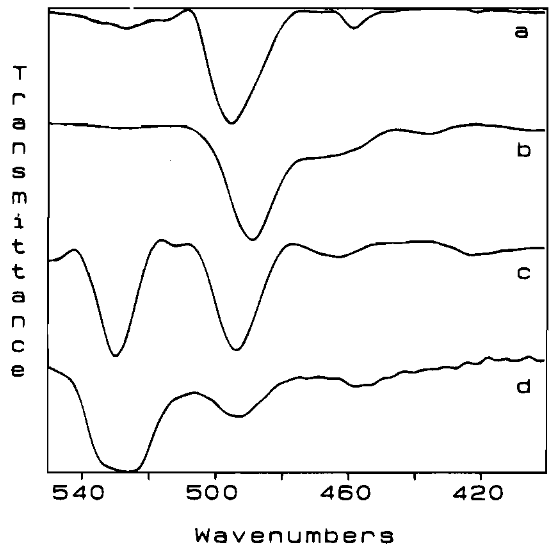

Figure 1. IR spectra of various polysulfide complexes in the region associated with ν_{SS}: $ZnS_6(MeIm)_2$ (a), ZnS_6(TMEDA) (b), $ZnS_6(DMAP)_2$ (c), $(PPh_4)_2[Zn(S_6)_2]$ (d).

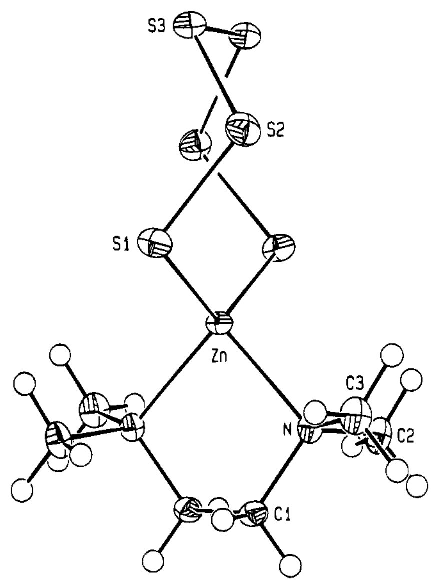

Figure 2. ORTEP plot of the non hydrogen atoms in ZnS_6(TMEDA).

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

$$Zn + {}^{6}/_{8}S_8 + 2L \rightarrow ZnS_6(L)_2 \qquad (2)$$

$$L = MeIm, Me_2NC_5H_4N, py, 0.5TMEDA$$

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 $ZnS_6(MeIm)_2$.[10] The yields are high, and the product purity is excellent. This species is air stable in solid state and can be recrystallized from MeIm upon the addition of nonpolar solvents. In these syntheses the grain size of the zinc was found to be important as was the stirring rate.

The Zn + S_8 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 $ZnS_6(DMAP)_2$ is an air and water stable yellow microcrystalline species. Its ^1H NMR spectrum is virtually unshifted vs the free ligand.[11] Its IR spectrum in the 600–400 cm^{-1} range closely resembles that for the structurally characterized ZnS_6(TMEDA) except for a ligand band at 525 cm^{-1} (Figure 1). $ZnS_6(DMAP)_2$ is a nonelectrolyte in DMF solution.

The complex $ZnS_6(py)_2$ has recently been reported to form from the py-Zn–S_8 reaction. We briefly checked these results since few preparative details were provided.[12] 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, $ZnS_6(py)_2$ is still of some preparative interest since the pyridine ligands are very labile.

The versatile species ZnS_6(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 CH_2Cl_2 solutions of ZnS_6(TMEDA) were stable under N_2 since we suspected the possibility of S-alkylation affording species such as S_xCH_2. In contrast to the TMEDA complex, most other ZnS_6L_2 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 CS_2.

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

Structure of ZnS_6(TMEDA). A crystallographic study of ZnS_6(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 $Zn(NO_2)_2$(TMEDA) which features O-bound nitrito

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ligands.[13] The bite angle of the polysulfide chelate is 119.73(2)°. The metrical details of the ZnS_6 ring are similar to those in $ZnS_6(MeIm)_2$ while the Zn−S distances resemble those seen in zinc thiolates.[14] An interesting feature is that the ring conformation of S_7 and the 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 S_4 array.[15] This long distance has been attributed to a repulsive interaction between the sulfur atoms associated with the 0° dihedral angle. In 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. $Zn(S\text{-}i\text{-}Pr)_2(MeIm)_2$.[16] In contrast, MeIm solutions of $ZnS_6(MeIm)_2$ and 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 S_3^- and has been observed previously in solutions of polysulfide anions (eqs 3 and 4).[17] Support for this assignment comes from

$$ZnS_6(TMEDA) + 6MeIm \rightleftharpoons Zn(MeIm)_6^{2+} + S_6^{2-} \quad (3)$$

$$S_6^{2-} \rightleftharpoons 2S_3^- \quad (4)$$

the observation of the same absorption maximum for MeIm solutions of $(PPh_4)_2S_6$. 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 S_6^{2-} from the coordination sphere of zinc. Using $(PPh_4)_2S_6$, we confirmed that in pyridine solutions S_6^{2-} dissociates into S_3^-. The nondisplacement of S_6^{2-} from ZnS_6L_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 with the result that $[Zn(py)_6]^{2+}$ is relatively less stable than $Zn(MeIm)_6^{2+}$ with respect to polysulfide ligation.[18]

The ability of MeIm to displace the polysulfide ligand is relevant to the oxygen sensitivity of MeIm solution of $ZnS_6(MeIm)_2$. Prolonged exposure of MeIm solutions of $ZnS_6(MeIm)_2$ to air converts the polysulfide complex into the orange-yellow crystals of $ZnS_2O_3(MeIm)_3$.[19] This water soluble zwitterionic species shows a ν_{SO} at 1163 cm^{-1}, typical of an S-bound thiosulfate complex.[20] The structure of $ZnS_2O_3(MeIm)_3$ was confirmed by single crystal X-ray diffraction. The oxidation of aqueous sulfide solution is known to give thiosulfate.[21,22]

Ligand Exchange Studies. Insights into the relative stability of the amine adducts were provided by ^{1}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}H NMR spectrum of $ZnS_6(MeIm)_2$ 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 methine 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. On the basis of the

$$ZnS_6(MeIm)_2 + 2py \rightleftharpoons ZnS_6(py)_2 + 2MeIm \quad (5)$$

$$K = [ZnS_6(py)_2][MeIm]^2/[ZnS_6(MeIm)_2][py]^2 \quad [py] = 11.3\ M \quad (6)$$

chemical shift data, we estimated (see Experimental Section) that the equilibrium constant for the displacement of *both* MeIm ligands by pyridine is $\sim 9 \times 10^{-6}$. In view of this small equilibrium constant it is understandable that attempts to prepare ZnS_6py_2 via ligand exchange from $ZnS_6(MeIm)_2$ would be unsuccessful, as was established by the fact that $ZnS_6(MeIm)_2$ can be recrystallized from pyridine solution.

^{1}H NMR studies revealed that (dimethylamino)pyridine (DMAP) completely displaced MeIm from $ZnS_6(MeIm)_2$ in pyridine-d_5 solution. The chemical shifts for TMEDA are insensitive to the effects of coordination, but preparative experiments demonstrated that TMEDA is a poorer donor toward ZnS_6 than MeIm but better than py. The trend in binding efficiencies is thus

$$DMAP > MeIm > TMEDA > py$$

which correlates with the basicity of the nitrogen donor ligand (Table 1). ^{1}H NMR studies showed that quinuclidine also displaces TMEDA from ZnS_6(TMEDA) giving $ZnS_6(quinuclidine)_2$.[24]

In addition to undergoing exchange with neutral donor ligands, ZnS_6(TMEDA) reacts with S_6^{2-} to give the known $Zn(S_6)_2^{2-}$.[25]

Acetylene Addition Reactions. Polysulfide complexes characteristically react with electrophilic acetylenes such as ester- and trifluoromethyl-substituted acetylenes.[26,27] The dim-

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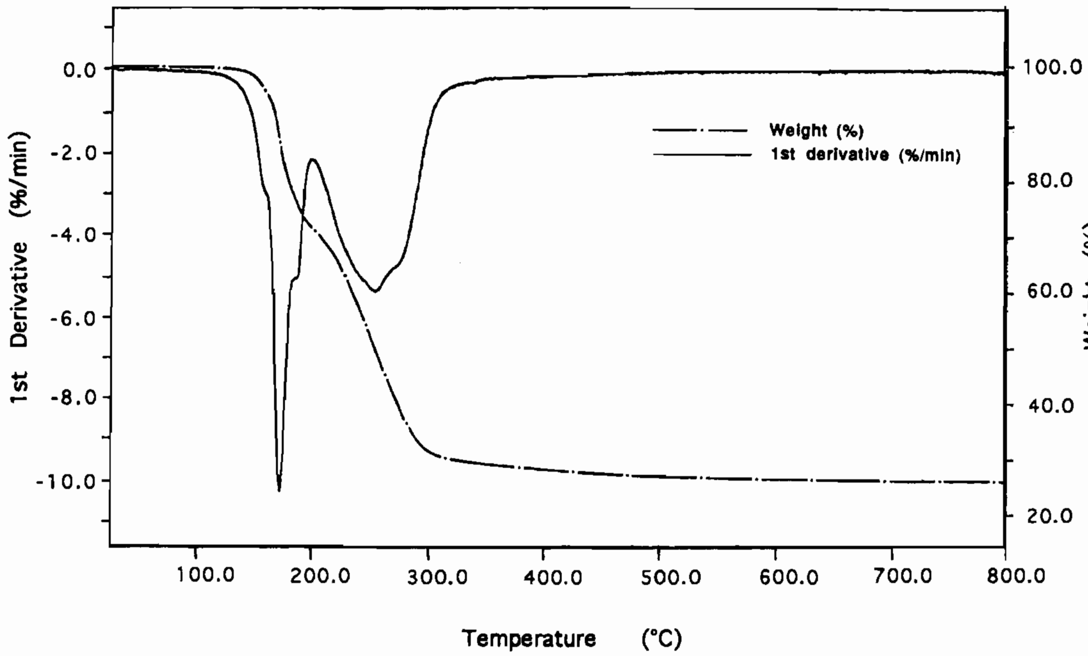
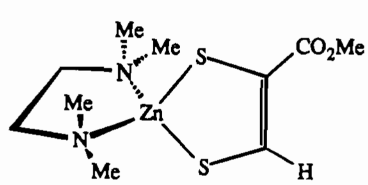


Figure 3. Thermogravimetric analysis of ZnS_6(TMEDA) under flowing He with a heating rate of 10 °C/min.

ethyl ester of acetylenedicarboxylic acid reacted readily with ZnS_6(TMEDA) to yield the dithiolene complex $ZnS_2C_2(CO_2Me)_2$(TMEDA). The light yellow microcrystalline solid shows three resonances in its ^{1}H NMR spectrum, indicative of a very simple structure. The IR spectrum is featureless in the ν_{SS} region; absorptions at 1720 and 1685 cm^{-1} are assigned to the ν_{CO} and $\nu_{C=C}$ 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 ZnS_2C_2H-(CO_2Me)(TMEDA). We observed no reaction between ZnS_6(TMEDA) and diphenylacetylene, dimethylfumarate, or norbornene.

The ^{1}H NMR spectrum of $ZnS_2C_2H(CO_2Me)$(TMEDA) features two peaks in the $N(CH_3)_2$ 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 ^{1}H NMR spectrum of this species remains essentially unchanged −35 °C. The N−Me sites could be equivalenced either via tetrahedral−square planar interconversion or an associative process.

Converison 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 ZnS_6(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 $ZnS_6(DMAP)_2$ shows the same pattern. The thermolysis of ZnS_6(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 ZnS_6(TMEDA) convert PBu_3 to $SPBu_3$ as indicated by ^{31}P NMR analysis of reaction solutions. When conducted on a preparative scale, treatment of ZnS_6(TMEDA) with 5 equiv of PBu_3 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 PBu_3 are employed we still observed, the formation of ZnS, although in diminished yields. For example the reaction of ZnS_6(TMEDA) with 2 equiv PBu_3 gave a 33% yield (theory: 40%) of ZnS together with unreacted starting complex. These experiments suggest that complexes of the type ZnS_x(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 ZnS_5(TMEDA) is more reactive toward PBu_3 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 ZnS_6(TMEDA) is thermodynamically unstable with respect to ZnS; hence, ZnS_6TMEDA is a kinetically stabilized intermediate in the reaction of Zn and S_8 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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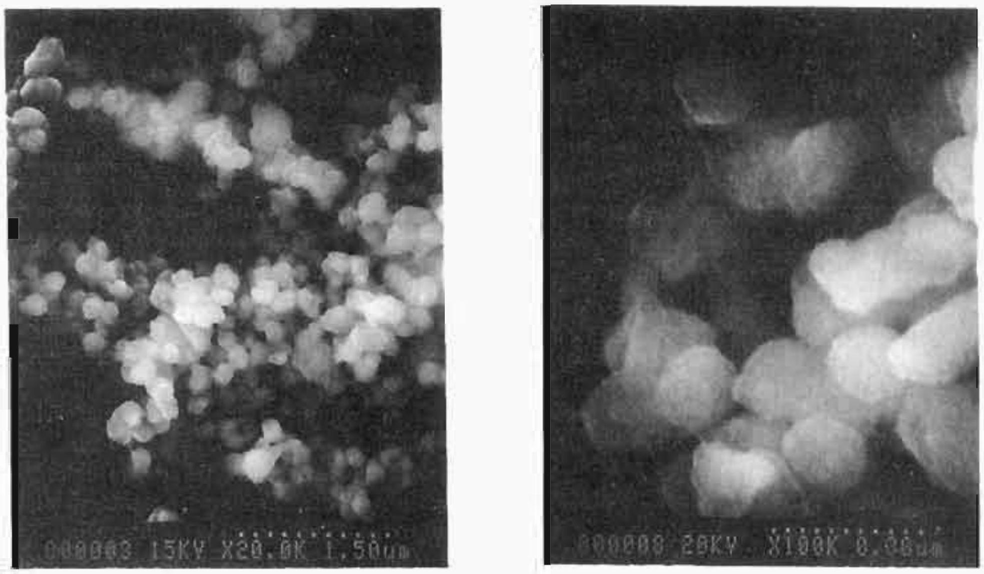
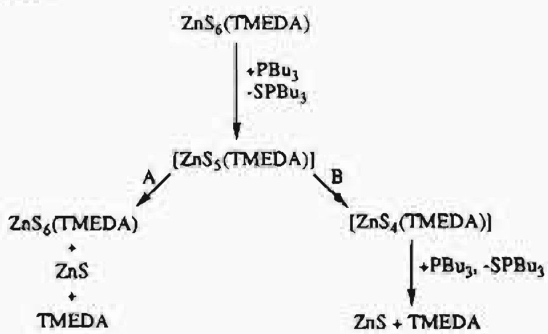


Figure 4. Scanning electron micrograph of ZnS produced by reaction of $ZnS_6(TMEDA)$ with PBu_3. The magnification is 20000× and 100000×, respectively.

Scheme 1



halogen.[28] the use of elemental sulfur as an oxidant is unusual.[3] Within the context of the L-M-S_8 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−S_8 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.[29] At the other extreme the py−Zn−S_8 reaction is extremely sluggish. The stability of ZnS_2N_2 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 thiolates.[30]

Strongly basic ligands displace the polysulfide ligand from ZnS_6L_2 as revealed by the formation of S_3^- which arises via the fragmentation of the displaced S_6^{2-} in polar solvents. The ability of MeIm, but not py, to displace the polysulfide parallels the results of the ligand competition studies and also reflects the added stability of complexes of the type $Zn(MeIm)_6^{2+}$. A consequence of polysulfide displacement is that solutions of ZnS_6L_2 in strong donor solvents exhibit enhanced reactivity toward oxygen, evidenced by our isolation of a thiosulfato complex.[14]

The most attractive complex for further studies is ZnS_6(TMEDA). This species forms in very high yields and is air 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 are soluble in a limited range of polar organic solvents.[25] An important advantage to ZnS_6(TMEDA) is that the diamine can be readily displaced by a variety of other ligands. Application of ZnS_6(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 ZnS_6L_2

$$\text{metal} + \text{elemental sulfur} \Longrightarrow \text{metal polysulfides} \Longrightarrow \text{metal sulfide} + \text{elemental sulfur} \quad (7)$$

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 PBu_3. This chemical method afforded submicron particles of ZnS. It is interesting that the desulfurization of ZnS_6(TMEDA) generates ZnS, even with substoichiometric amounts of PBu_3. These experiments suggest that ZnS formation occurs via aggregation of ZnS_x species where $x < 6$. Further studies along these lines may identify new Zn−S clusters.[31]

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 CaH_2. 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'*-Tetramethylethylenediamine (TMEDA), 4-(*N,N*-dimethylamino)pyridine (DMAP), dimethyl acetylenedicarboxylate (DMAD), and methyl propiolate were obtained from Aldrich and used as received. $(PPh_4)_2S_6$ was prepared by the addition

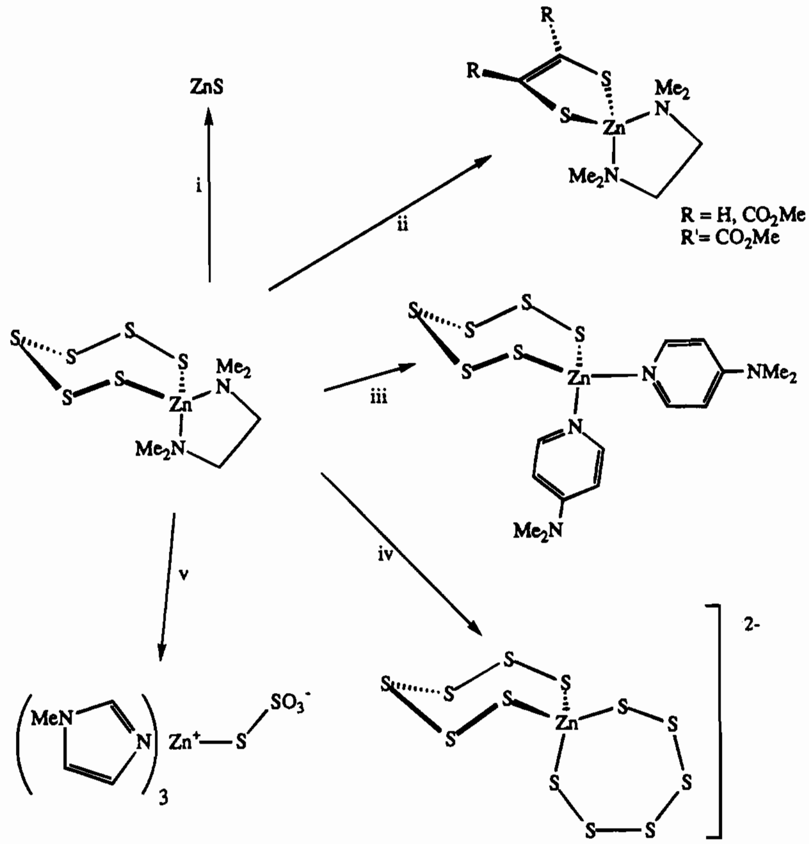
(27) One early example of many: Ducelliez, F. *Bull. Soc. Chim. Fr.* **1913**, *13*, 815.

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

(29) Berg, J. M. *Prog. Inorg. Chem.* **1989**, *38*, 143.

(30) Leading references: Dance, I.; Fisher, K. *Prog. Inorg. Chem.* **1994**, *41*, 637. Dance, I. G. *Polyhedron* **1986**, *5*, 1037. Herron, N.; Calabrese, J. C.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426.

Scheme 2



Conditions: (i) 350 °C; (ii) $C_2(CO_2Me)R$ (R = H, CO_2Me); (iii) $Me_2NC_5H_4N$; (iv) $(PPh_4)_2S_6$; (v) MeIm, O_2.

of a slurry of 1.57 g of PPh_4Cl in 20 mL of H_2O to a solution of 0.135 g of S_8 and 0.51 g of $Na_2S.9H_2O$ in 10 mL of H_2O.

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.

$ZnS_6(MeIm)_2$. A suspension 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 Et_2O and stored at −5 °C. After 6 h the resulting yellow powder was filtered out and washed with Et_2O. The crude product was extracted into ~70 mL of MeIm which was diluted with ca. 100 mL of Et_2O. Yield: 17.2 g (75%). Anal. Calcd for $C_8H_{12}N_4S_6Zn$: C, 22.77; H, 2.87; N, 13.28; S, 45.58; Zn, 15.49. Found: C, 23.22; H, 2.93; N, 13.63. IR (KBr): 495 cm^{-1} (ν_{SS}).

ZnS_6(TMEDA). A Schlenk flask was charged with 2.61 g of zinc dust (39.9 mmol), 7.791 g of sulfur (243 mmol), and 100 mL of TMEDA. The reaction mixture was stirred at 90 °C for ca. 2 h to give a yellow suspension. After cooling to room temperature, the suspension was diluted with ca. 100 mL of Et_2O and cooled at −5 °C. After a few hours the yellow precipitate was collected and washed with Et_2O. The product was recrystallized by extraction with ca. 100 mL of CH_2Cl_2 followed by dilution with ca. 125 mL of Et_2O. Yield: 9.69 g (75%). Anal. Calcd for $C_6H_{16}N_2S_6Zn$: C, 19.26; H, 4.31; N, 7.49. Found: C, 19.37; H, 4.32; N, 7.44. ^1H NMR (pyridine-d_5): δ 2.40 (s, 4H), 2.19 (s, 12H). IR (KBr): 489 cm^{-1} (ν_{SS}).

$ZnS_6(DMAP)_2$. A mixture of 0.655 g of zinc dust (10 mmol), 1.947 g of sulfur (60.7 mmol), and 2.463 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 Et_2O. The resulting yellow solid was collected and washed with 3 × 20 mL portions of Et_2O. The crude product was recrystallized from DMF and ether. Yield: 3.87 g (77%). Anal. Calcd for $C_{14}H_{20}N_4S_6Zn$: C, 33.47; H, 4.02; N, 11.16; S, 38.32; Zn, 13.03. Found: C, 33.05; H, 4.01; N, 11.10; S, 37.10; Zn, 13.01. ^1H NMR (pyridine-d_5): δ 8.37 (d, 2H), 6.45 (d, 2H), 2.72 (s, 6H): IR (KBr): 494 cm^{-1} (ν_{SS}).

$ZnS_6(py)_2$. 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 Et_2O. The crude product was filtered and recrystallized from pyridine/Et_2O and washed with Et_2O followed by CS_2. Yield: 8.37 g (50%). Anal. Calcd $C_{10}H_{10}N_2S_6Zn$: C, 28.87; H, 2.42; N, 6.74. Found: C, 28.73; H, 2.41; N, 6.62.

ZnS_6(quinuclidine)$_2$. A Schlenk flask was charged with 0.298 g of ZnS_6(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 50 mL of Et_2O, the resulting yellow solid was filtered out, washed with Et_2O, and dried under vacuum. Yield: 0.290 g (75%). The NMR spectrum of a sample in py-d_5 solution showed ~1% of ZnS_6(TMEDA). ^1H NMR (pyridine-d_5): δ 2.3 (t, 12H); 1.54 (septet, 2H); 1.34 (m, 12H). IR (KBr): 492 cm^{-1} (ν_{SS}).

$(PPh_4)_2[ZnS_{12}]$.[25] To a mixture of 0.331 g of ZnS_6(TMEDA) (0.38 mmol) and 0.144 g of $(PPh_4)_2S_6$ (0.38 mmol) in a 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 Et_2O. The yellow microcrystalline solid was washed with several portions of Et_2O and dried under vacuum. Yield: 0.34 g (78%). Anal. Calcd for $C_{48}H_{40}P_2S_{12}Zn$: C, 51.07; H, 3.57; P, 5.49; S, 34.08; Zn, 5.79. Found: C, 50.83; H, 3.46; P, 5.06; S, 32.64; Zn, 5.18.

$Zn(S_2O_3)(MeIm)_3$. Dry air was passed over a solution of 0.406 g of $ZnS_6(MeIm)_2$ (0.96 mmol) in 4.5 mL of MeIm for ca. 70 h. The resulting dark red supernatant was decanted, leaving a pink-yellow residue which was washed with 4 mL of cold MeIm and finally with toluene. Yield: 0.138 g (34%). Anal. Calcd for $C_{12}H_{18}N_6O_3S_2Zn$: C, 34.01; H, 4.28; N, 19.83. Found: C, 33.55; H, 4.53; N, 19.53. IR (KBr): 1163 cm^{-1} (ν_{so}).

$ZnS_2C_2(CO_2Me)_2(TMEDA)$. A solution of 0.226 g of ZnS_6(TMEDA) (0.6 mmol) in 6 mL of warm THF was treated with 220 μL of dimethyl acetylenedicarboxylate (1.8 mmol). The yellow reaction mixture was stirred at room temperature for 9 h and then filtered. The orange-yellow solid residue was washed with small portions of cold THF and hexane to afford $ZnS_2C_2(CO_2Me)_2$(TMEDA) as a light yellow colored solid. Yield: 0.107 g (46%). Anal. Calcd for $C_{12}H_{22}N_2O_4S_2Zn$: C, 37.16; H, 5.72; N, 7.22; S, 16.53; Zn, 16.86. Found: C, 37.20; H, 5.77; N, 7.21; S, 16.40; Zn, 16.72. ^{1}H NMR (CD_3CN): δ 3.63 (s, 6H), 2.84 (s, 4H), 2.52 (s, 12H). IR (KBr): 1720 (ν_{CO}), 1685 cm^{-1} ($\nu_{C=C}$).

$ZnS_2C_2H(CO_2Me)(TMEDA)$. A solution of 1.381 g of ZnS_6(TMEDA) (3.7 mmol) in 25 mL of warm THF was treated with 1.5 mL of methyl propiolate (16.8 mmol), and the reaction mixture was allowed to stir at 60 °C for ca. 19 h. After cooling to room temperature, the solvent layer was decanted. The yellow residue was washed with 5 mL of cold THF followed by 10 mL portions of hexane. Yield: 0.502 g (42%). Anal. Calcd for $C_{10}H_{20}N_2O_2S_2Zn$: C, 36.42; H, 6.11; N, 8.50; S, 19.44; Zn, 19.83. Found: C, 36.28; H, 6.05; N, 8.01; S, 18.97; Zn, 18.13. ^{1}H NMR (CD_3CN): δ 7.8 (s, 1H), 3.62 (s, 3H), 2.82 (s, 4H), 2.52 (s, 12H). IR (KBr): 1692 (ν_{CO}), 1680 (sh, $\nu_{C=C}$).

Thermal Decomposition of ZnS_6(TMEDA). A porcelain boat, charged with 0.506 g (1.35mmol) of ZnS_6(TMEDA), was loaded into a tube-furnace. The temperature was first raised gradually to 500 °C under a continuous flow of nitrogen. After 1 h the temperature was increased to 600 °C where it was maintained for 26 h and then cooled slowly under nitrogen. The 0.131 g of white-gray residue corresponds to 25.9% yield of the starting material (theoretical weight yield is 26.01%). Anal. Calcd for ZnS: S, 32.91; Zn, 67.09. Found: S, 32.27; Zn, 67.77.

^{1}H NMR Studies on Pyridine-d_5 Solutions of $ZnS_6(MeIm)_2$. The $ZnS_6(MeIm)_2$ samples for ^{1}H NMR studies were prepared by dissolving varying amounts of $ZnS_6(MeIm)_2$ in 0.5 mL of pyridine-d_5. Spectra were recorded at 19−20 °C (see Figure 3). The equilibrium constant was estimated on the basis of the following three assumptions: 1. The chemical shift for the 2H signal of $ZnS_6(MeIm)_2$ was assumed to be 8.05 ppm (1610 Hz). The was determined by visual inspection, with an estimated error of 5%. 2. The chemical shift of 2H signal for MeIm was assumed to be the same for both $ZnS_6(MeIm)_2$ and ZnS_6(MeIm)(py). 3. The concentration of pyridine was unchanged throughout the concentration range. The equilibrium constant takes the following form:

$$K = [ZnS_6py_2][MeIm]^2/[ZnS_6(MeIm)_2][py]^2$$

Let x = $[ZnS_6py_2]$ and let $[Zn]_o$ = the total zinc concentration: then

$$K = (x)(2x)^2/([Zn]_o - x)[py]^2$$

We then consider the special case where MeIm is half-dissociated, i.e. $x = 0.5[Zn]_o$:

$$K = (0.5[Zn])([Zn]_o)^2/(0.5[Zn]_o)[py]^2 = [Zn]_o^{\,2}/[py]^2$$

This special case occurs (see Figure 3) when $[Zn]_o$ = 0.033 M. [py-d_5] = 11.3 M, and [py-d_5]^2 = 128 M^2, giving

$$K = 8.5 \times 10^{-6}$$

Table 2. Crystallographic Parameters of ZnS_6(TMEDA)

formula	$C_6H_{16}N_2S_6Zn$
molecular mass	373.94
cryst dimens, mm	0.1 × 0.2 × 0.6
temp, °C	−75
cryst system	monoclinic
space group	$C2/c$ (C^6_{2h}) (No. 15)
unit cell	
a, Å	12.255(3)
b, Å	10.559(2)
c, Å	12.392(2)
α, γ, deg	90
β, deg	110.22(2)
V, Å^3	1505(10)
calcd density, g/cm^3	1.650
Z	4
μ, cm^{-1}	24.46
radiation (λ, Å)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4 automated κ-axis scan
range 2θ, deg	2−56
scan mode	ω/θ
measd reflcns	2077
unique reflcns	1817
R_i, %	1.9
transm (min, max)	0.609, 0.787
R, R_w, %	2.2, 2.6
largest resids, e·Å^{-3}	+0.33, −0.31

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 facial boundaries were 0.05, 0.07, 0.08, and 0.27 mm, respectively. The structure was solved by direct methods, SHELXS-86. The correct positions of all non-H atoms were deduced from an E-map. A subsequent least-squares refinement and difference Fourier synthesis revealed positions for the H atoms. In the final cycle of the least-squares refinement, all positions were independently refined. Anisotropic thermal coefficients were refined for non-H atoms, isotropic thermal coefficients were refined for H atoms, and an empirical isotropic extinction parameter was varied. Successful convergence was indicated by the maximum shift/error for the last cycle. The highest peaks in the final difference Fourier map were in the vicinity of the Zn and S atoms; the final map had no other significant features. A final analysis of the variance between the observed and the calculated structure factors showed no systematic errors.

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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.

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