

between the gas-phase and solution processes is associated with solvent interactions on the TS and reactants. The solution TS structure, in accordance with the Hammond postulate,²² now resembles To^- , and thus a share of the activation energy required for OH^- attack on the amide is associated with structural changes accompanying rehybridization at N in much the same way as is responsible for the barrier to rotation in formamide.^{6,9} Amides in which the structure predisposes the amidic unit toward a pyramidal N with attendant lengthening of the C-N bond are accordingly activated toward nucleophilic attack and exhibit an accelerated hydrolysis.²³

This structural distortion amounts to destabilization of the ground state with concomitant reduction in the TS barrier for OH^- attack. We¹²⁻¹⁵ and others²⁴ have previously attributed the activation to a distortion that removes amidic resonance. However, structural distortion cannot remove resonance interactions if they are not present in the first place.^{6,9} Our structural studies with **4** and **5** are consistent with the theoretical predictions.⁶ Furthermore, the kinetic results suggest that there is no straightforward relationship between the degree of rotation about the N-C(O) bond and the kinetic reactivity toward OH^- . Rather, there is a direct relationship between (a) the extent of N pyramidalization and (b) N-C(O) lengthening and k_{OH^-} .²⁵

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(21) (a) Guthrie, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 3608; (b) *Acc. Chem. Res.* **1983**, *16*, 1222.

(22) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 3608. (b) Farcasiu, D. *J. Chem. Educ.* **1975**, *52*, 76.

(23) Energetically, the accelerated hydrolysis of distorted amides appears as a reduction in the ΔG^\ddagger for OH^- attack and thus depends on a reduction in ΔH^\ddagger and/or a less negative ΔS^\ddagger . Since the entropy term plays a large part in amide hydrolysis,^{5,21} changes in this with increasing distortion may play a large role in the observed acceleration (work in progress).

(24) **4a** was originally prepared by Blackburn et al.: Blackburn, G. M.; Skaife, C. J.; Kay, I. T. *J. Chem. Res., Miniprint* **1980**, 3650.

(25) Note Added in Proof. It remains to be established whether the computed situation for formamide obtains for more heavily substituted amides. Work in progress in these laboratories addresses the adequacy of the resonance model in explaining the physicochemical properties of these and other amides.

Direct Approaches to Zinc Polychalcogenide Chemistry: $\text{ZnS}_6(\text{N-MeIm})_2$ and $\text{ZnSe}_4(\text{N-MeIm})_2$

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We describe new and efficient routes to zinc chalcogenides that involve the solution-phase reactions of zinc metal with sulfur, organic disulfides, and selenium.¹ Our findings further establish the remarkable reactivity of *N*-alkylimidazole solutions of chalcogen compounds toward metals² and as well as metal sulfides. Zinc sulfides (and selenides) are widely used as phosphors, semiconductors, long-wavelength windows, and catalysts.³ Zinc

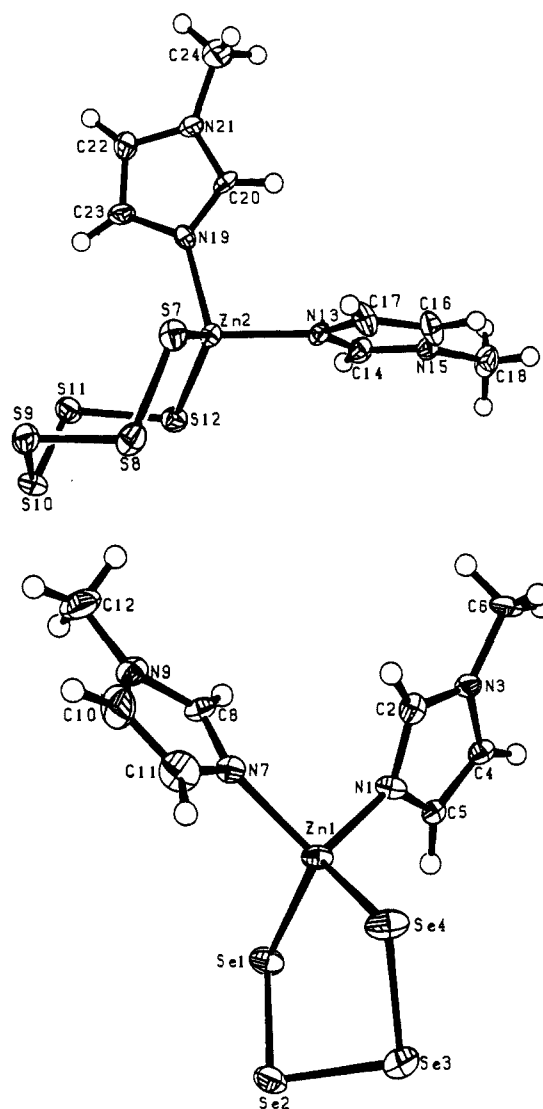


Figure 1. The structures of $\text{ZnS}_6(\text{N-MeIm})_2$ (**1**) (top) and $\text{ZnSe}_4(\text{N-MeIm})_2$ (**2**) (bottom) with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg) for **1**: Zn-S7, 2.312 (3); S7-S8, 2.048 (4); S8-S9, 2.043 (4); S9-S10, 2.058 (4); S10-S11, 2.047 (4); S11-S12, 2.044 (4); S12-Zn, 2.290 (3); N19-Zn, 2.014 (7); N13-Zn, 2.045 (7); N19-Zn-N13, 103.0 (3); S7-Zn-S12, 121.1 (1). Selected bond distances (Å) and angles (deg) for **2**: Zn-Se1, 2.431 (2); Se1-Se2, 2.330 (2); Se2-Se3, 2.333 (2); Se3-Se4, 2.345 (2); Se4-Zn, 2.430 (2); Zn-N1, 2.023 (10); Zn-N7, 2.021 (7); Se1-Zn-Se4, 111.56 (7); N1-Zn-N7, 101.0 (4).

mercapto imidazole complexes occur widely in biological systems.⁴

Zinc dust (1.10 g, 16.83 mmol) was found to dissolve in a hot (100 °C) *N*-methylimidazole (*N*-MeIm, 20 mL) solution of elemental sulfur (3.25 g, 101.37 mmol). Over the course of 12 h, the reaction proceeded to give a clear, greenish-brown solution. The zinc dissolved *completely* in this reaction; we did not observe the formation of ZnS. The cooled, filtered solution was layered with toluene (40 mL), and after 24 h at 0 °C bright yellow crystals of $\text{ZnS}_6(\text{N-MeIm})_2$ (**1**) were collected (3.69 g).⁵ Yields ranged

(3) A selection of recent references on the synthesis and applications of zinc sulfides: Osakada, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1117. Yao, G. Q.; Shen, H. S.; Honig, E. D.; Kershaw, R.; Dwight, K.; Wold, A. *Solid State Ionics* **1987**, *24*, 249. Yanagida, S.; Ishimaru, Y.; Miyake, Y.; Shiragami, T.; Pac, C.; Hashimoto, K.; Sakata, T. *J. Phys. Chem.* **1989**, *93*, 2576. Kortan, A. R.; Hull, R.; Opila, B.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327. Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 431.

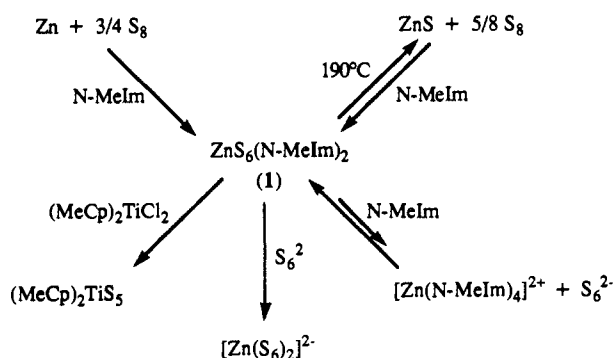
(4) Berg, J. M. *Prog. Inorg. Chem.* **1988**, *37*, 143.

(5) Anal. Calcd for $\text{C}_8\text{H}_{12}\text{N}_4\text{S}_6\text{Zn}$ (found): C, 22.80 (22.92); H, 2.87 (2.95); N, 13.27 (13.44); S, 45.59 (45.49); Zn, 15.49 (15.26). IR (KBr, cm^{-1}): 1111, 497, 459.

(1) Reviews of polychalcogenide complexes: Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742; *Angew. Chem.* **1985**, *97*, 745. Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223.

(2) Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043.

Scheme I



from 50 to 60%. Both 325-mesh zinc powder (Cerac) and conventional zinc dust (Mallinckrodt) have been successfully employed in this reaction.

N-MeIm solvent is crucial to the reactivity of the zinc powder, and no reaction was observed for *tert*-butylpyridine/Zn/S₈ or toluene/Zn/S₈ at 100 °C for 12 h. A solution of sulfur in 1,2-dimethylimidazole (1,2-Me₂Im), zinc dust, and sulfur afforded green-yellow crystals analyzing as ZnS₆(1,2-Me₂Im)₂.⁶

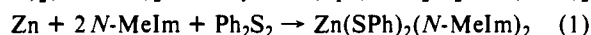
A crystallographic study⁷ of **1** shows that zinc is situated in tetrahedral N₂S₂ environment⁸ (Figure 1). The Zn-S distances are 2.290 (3) and 2.312 (3) Å. The ZnS₆ ring conformation resembles that for *c*-S₇.⁹ In this respect, the ZnS₆ ring in **1** is similar to that in (PPh₄)₂[Zn(S₆)₂].^{10,11} In fact, the latter binary zinc sulfide anion can be prepared by treatment of DMF solutions of **1** with (PPh₄)₂S₆ followed by Et₂O precipitation.¹²

Solutions of **1** in *N*-MeIm are blue-green with λ_{max} = 618 nm. We propose that this color arises from polysulfide anion radicals, e.g., S₃⁻, which are known to exist in equilibrium with free S₆²⁻.¹³ *N*-MeIm solutions of (PPh₄)₂S₆ (1.72 × 10⁻⁴ M) and **1** (2.9 × 10⁻² M) display comparably intense absorptions at 618 nm. Thus at 2.9 × 10⁻² M in **1**, approximately 1% of the polysulfide anion is uncoordinated. As indicated in Scheme I, *N*-MeIm is proposed to displace the polysulfide, giving [Zn(*N*-MeIm)₄]²⁺. These findings are relevant to the action of zinc catalysts for the addition of polysulfur radicals to polyolefins in the vulcanization process.¹⁴ Reaction of an acetone solution of **1** with (MeCp)₂TiCl₂ gave (MeCp)₂TiS₅ in 90% yield;¹⁵ thus it appears that, as with other zinc chalcogenides,¹⁶ **1** may be a useful source of S_x²⁻.

Compound **1** decomposes at 190 °C in a vacuum, leaving an off-white residue of ZnS. Further studies on the relationship

between **1** and ZnS have revealed an unexpected aspect of *N*-MeIm/S₈ reactivity. We found that an *N*-MeIm suspension of freshly precipitated ZnS¹⁷ dissolved (minutes, 100 °C) upon addition of elemental sulfur (5 mol of S/mol of ZnS). This novel reactivity was found to depend on the morphology of the solid. Crystalline ZnS (hexagonal or cubic) appears unreactive toward S₈/*N*-MeIm, in contrast to samples characterized by broad diffraction peaks (fwhm 2θ_{28.5} ~ 2.8°). The most reactive forms of zinc sulfide are the "organosols". Such colloidal species¹⁷ dissolve in seconds (25 °C) upon the addition of *N*-MeIm/S₈ to give **1**. *N*-MeIm solutions of sulfur also dissolve freshly precipitated sulfides of Mn, Fe, Ni, and Cu. This finding suggests that metal sulfides may be intermediates in *N*-MeIm/M/S₈ reactions.

N-MeIm solutions of organodichalcogenides are also reactive toward metal powders. For example, zinc dust (0.82 g) dissolved completely in *N*-MeIm (15 mL) upon addition of 1 equiv of Ph₂S₂ (100 °C, 12 h). Ether precipitation gave colorless crystals of Zn(SPh)₂(*N*-MeIm)₂ in 68% yield¹⁹ (eq 1). Ph₂Se₂ and (*i*-PrS)₂



in *N*-MeIm have also been found to dissolve zinc; *N*-MeIm/Ph₂S₂ dissolves iron, nickel, and copper.²⁰ This approach has considerable synthetic potential.²¹

The *N*-MeIm/Zn/Se reaction (100 °C, 18 h) gave a reddish-brown solution, which upon layering with THF afforded a 30% yield of ZnSe₄(*N*-MeIm)₂ (**2**).²² The molecular structure²³ of **2** consists of a tetrahedrally coordinated Zn ion and a nonplanar ZnSe₄ ring²⁴ (Figure 1). The occurrence of a smaller ZnE_n ring for E = Se vs E = S is an established trend attributable to the increased size of the heavier chalcogen. The *N*-MeIm/Zn/Se reaction is noteworthy because it employs the less reactive (gray) allotrope of selenium.

In summary, *N*-MeIm suspensions of zinc exhibit particularly well behaved reactivity toward sulfur. This reactivity has been extended to include organic disulfides and elemental selenium. The finding that metal sulfides themselves are reactive toward *N*-MeIm/S₈ defines a number of opportunities that interrelate materials science and coordination chemistry of metal chalcogenides.

Acknowledgment. This research was supported by the National Science Foundation through Grants CHE-87-11460 and DMR-89-20538.

Supplementary Material Available: X-ray diffraction patterns for ZnS and elemental analysis, thermal gravimetric trace for **1**, and tables of bond distances and angles, atomic positions, and thermal parameters for **1** and **2** (13 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

(6) Anal. Calcd for C₁₀H₁₆N₄S₆Zn (found): C, 26.69 (27.34); H, 3.58 (3.75); N, 12.45 (12.65); S, 42.75 (41.71); Zn, 14.53 (14.38). IR (KBr, cm⁻¹): 1147, 499, 443.

(7) ZnS₆(*N*-MeIm)₂ crystallizes from *N*-MeIm/toluene in the triclinic space group P1̄ with α = 96.45 (2)°, β = 99.66 (4)°, γ = 90.33 (4)°, a = 7.434 (4) Å, b = 13.718 (3) Å, c = 16.339 (3) Å, Z = 2, and ρ_{calcd} = 1.717 g/cm³. With Mo Kα radiation, 5992 reflections were collected at -75 °C of which 2805 were observed (I > 2.58σ(I)). The structure was solved by direct methods (SHELX-86) and refined to a final R = 0.047 and R_w = 0.044.

(8) The coordination environment resembles that in Zn(SC₆H₂-2,4,6-*i*-Pr₃)₂(imidazole)₂: Corwin, D. T., Jr.; Koch, S. A. *Inorg. Chem.* **1988**, *27*, 493.

(9) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 147.

(10) Müller, A.; Schimanski, J.; Schimanski, U.; Bögge, H. *Z. Naturforsch.* **1985**, *40B*, 1277.

(11) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24.

(12) Anal. Calcd for C₄₈H₄₀P₂S₁₂Zn (found): C, 51.06 (51.25); H, 3.58 (3.72); S, 34.01 (33.92); Zn, 5.79 (5.57).

(13) Discussions of the optical properties of polysulfide radical anions: Chivers, T. In *Homoatomic Rings, Chains, and Macromolecules of the Main Group Elements*; Rheingold, A. L., Ed.; Elsevier: New York, 1977; pp 499-537. Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1983**, *22*, 290. Chivers, T.; Edelmann, F.; Richardson, J. F.; Schmidt, K. J. *Can. J. Chem.* **1986**, *64*, 1509. Cotton, F. A.; Harmon, J. B.; Hedges, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 1417. Also see: Seel, F. in ref 14, pp 67-89.

(14) McCleverty, J. A. In *Sulfur*; Müller, A.; Krebs, B., Eds.; Elsevier: Amsterdam, 1984; p 311.

(15) Darkwa, J.; Giolando, D. M.; Murphy, C. J.; Rauchfuss, T. B. *Inorg. Synth.* **1990**, *27*, 51.

(16) Yang, X.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1990**, 34.

(17) "Poorly crystalline" cubic ZnS was prepared (a) by the reaction of H₂S and Zn(OAc)₂·2H₂O (4.01 g) in DMF (50 mL) followed by dilution with methanol (150 mL) and (b) by the reaction of H₂S with aqueous Zn(OAc)₂·2H₂O. After vacuum drying at 100 °C, these samples were examined by microanalysis and X-ray powder diffraction.

(18) These species are prepared by the reaction of H₂S with DMF solutions of Zn(OAc)₂·2H₂O: Dev, S.; Taniguchi, A.; Yamamoto, T.; Kubota, K.; Tominaga, Y. *Colloid Polym. Sci.* **1987**, *265*, 922.

(19) Anal. Calcd for C₂₀H₂₂N₄S₂Zn (found): C, 53.63 (53.63); H, 4.95 (4.88); N, 4.95 (4.88); S, 14.32 (14.27); Zn, 14.60 (14.66). IR (KBr, cm⁻¹): 1577, 740, 424.

(20) Dev, S.; Rauchfuss, T. B.; Stern, C. L., unpublished results.

(21) Toluene solutions of Ph₂S₂ are known to dissolve several metalloids (Sn, Ti, In) but this reactivity does not apply to transition metals; see: Kumar, R.; Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1988**, 1045.

(22) Anal. Calcd for C₈H₁₂N₄Se₄Zn (found): C, 17.62 (18.45); H, 2.22 (2.38); N, 10.27 (10.65); Se, 57.91 (56.33); Zn, 11.98 (11.67). IR (KBr, cm⁻¹): 1092. Complex **2** was insufficiently soluble in DMF for ⁷⁷Se NMR studies.

(23) ZnSe₄(*N*-MeIm)₂ crystallizes from *N*-MeIm/THF in the monoclinic space group P2₁/c with α = 90° and β = 102.49 (4)°, a = 7.400 (3) Å, b = 27.575 (6) Å, c = 15.199 (7) Å, Z = 8 and ρ_{calcd} = 2.393 g/cm³. With Mo Kα radiation, 5760 reflections were collected at -75 °C of which 2949 were observed (I > 2.58σ(I)). The structure was solved by direct methods (SHELX-86) and refined to R = 0.042 and R_w = 0.046.

(24) The ZnSe₄ ring is also seen in (PPh₄)₂[Zn(Se₄)₂]: Adel, J.; Weller, F.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43B*, 1094.