Zinc Polysulfides as Precursors to ZnS and as Group Transfer Reagents

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ZnS is an important material which is widely used in pigments, semiconductors, rubber compounding and phosphors [1]. We have developed a new entry into zinc sulfide chemistry that involves the reaction of elemental zinc and sulfur in a donor solvent. This is the “L-M-X” approach, where L = N-donor, M = metal in zero oxidation state, and X = oxidant; in our case S₈ (eq : ) [2].

\[
\text{Zn} + \frac{6}{8} \text{S}_8 + 2 \text{L} \xrightarrow{\Delta} \text{ZnS}_6\text{L}_2
\]

(1)

Using this methodology, we have prepared a wide variety of ZnS₆(N-donor)₂ species. These reactions can be conducted safely on a substantial scale (>50 g). Depending on the identity of L, these complexes display a range of reactivity, solubility, and stability. Crystallographic analysis shows that ZnS₆(TMEDA) adopts a tetrahedral geometry with a seven-membered ZnS₆ ring [3].

Ligand competition studies on solutions of ZnS₆L₂ complexes revealed that their relative stability (DMAP>MeIm>TMEDA>pyridine) parallels the basicity of the ligands. For example, TMEDA is displaced by the more basic ligands MeIm (pKₐ = 7.33) and quinuclidine (pKₐ = 10.95), but not by pyridine (pKₐ = 5.23). On the other hand, the very labile pyridine analog, ZnS₆Py₂, is a useful precursor to adducts of more specialized donors, such as TEEDA (N,N,N',N' -tetraethylthielenediamine) and (-)sparteine, which can not be prepared by direct L/Zn/S₈ reactions. Crystallographic analysis of ZnS₆{(-)-sparteine} indicates it to be a mixed-crystal complex best described as [ZnS₆{(-)-sparteine}][0.₈[ZnS₅{(-)-sparteine}][0.₂]. Optical and reactivity studies showed that MeIm, but not pyridine, displaces the polysulfide from ZnS₆(MeIm)₂ as indicated by the appearance of the chromophore S₃⁻. ZnS₆(TMEDA) engages in conventional reactions with S₆²⁻ (to give ZnS₁₂²⁻) and electrophilic acetylides (to give the dithiolene complexes).

Solid ZnS₆(TMEDA) cleanly decomposes into ZnS at 350 °C as indicated by TGA and preparative scale studies. Thus, these polysulfides represent donor-stabilized intermediates in the reaction of sulfur and zinc:

Submicron cubic ZnS is generated upon partial desulfurization of ZnS₆(TMEDA) with tertiary phosphines (eq 2) as established by electron microscopic studies.

\[
\text{ZnS}_6(\text{TMEDA}) + 5 \text{PBU}_3 \xrightarrow{} \text{ZnS} + 5 \text{Bu}_3\text{PS} + \text{TMEDA}
\]

(2)

The reaction of ZnS₆(MeIm)₂ with 5 equiv of zinc dust affords nanosize material ZnS(MeIm)₁₋ₓ (x = 0 - 0.3). Unlike cubic ZnS, this species is very reactive towards MeIm solutions of sulfur to afford ZnS₆(MeIm)₂. This result suggests that the nanosize material is an intermediate in the formation of ZnS₆(MeIm)₂ from the reaction of zinc, sulfur, and MeIm. Its formulation is supported by TGA, XPS, CL, and SS MAS ¹³C NMR spectroscopic measurements. The ZnS(MeIm)₁₋ₓ species also reacts with Cu₄S₁₀(MeIm)₄ [4c] to afford [Zn(MeIm)₆][Cu₄S₁₂).

The species ZnS₆(TMEDA) is a potent polysulfido-transfer reagent. The reaction of this zinc reagent with Cp₂TiCl₂ gives Cp₂TiS₅, which is a widely cited polysulfido-group transfer reagent itself [5]. Treatment of a Cs₂ slurry of ZnS₆(TMEDA) with Se₂Cl₂ gives 1,2-
Se$_2$S$_6$, as confirmed by reverse phase HPLC, Raman, and $^{77}$Se NMR spectroscopic measurements (eq 3) [5].

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{Zn} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\text{Me} & \quad \text{Me}
\end{align*}
\xrightarrow{\text{Se}_2\text{Cl}_2, \text{CS}_2, -30^\circ \text{C}}
\begin{align*}
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\text{Se}_{\text{Zn}} & \quad \text{Se}_{\text{Zn}} \\
\text{ZnCl}_2(\text{TMEDA})
\end{align*}
\text{ (3)}

The reaction of CH$_2$Cl$_2$ solutions of ZnS$_6$(TMEDA) with TiCl$_4$ affords a brown solid TiS$_x$ (x~10). Unlike other titanium sulfides, this material is soluble in donor solvents. Extraction of TiS$_x$ with Melm affords the molecular complex Ti(S$_2$)$_2$(Melm)$_3$, which can be considered a Lewis base adduct of Ti(S$_2$)$_2$. Crystallographic analysis reveals a pseudo trigonal-bipyramidal geometry around Ti, with the two of the Melm ligands occupying axial sites. Solutions of TiS$_4$(Melm)$_3$ are extremely sensitive to air. Oxygenation generates the dinuclear μ-oxo species [Ti$_2$(S$_2$)$_2$(μ-S$_2$)(μ-O)(Melm)$_4$], as confirmed by single crystal X-ray diffraction.

References

(c) Phoenix, K. A.; Skrable, K. W.; Chabot, G. E.; French, C. S.; Jo, M.; Falo, G. A. Health Phys. 1993, 64, 64.


