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 S_8 (eq 1) [2].

$$Zn + 6/8\ S_8 + 2\ L \xrightarrow{\ \Delta\ } ZnS_6L_2 \qquad\qquad (1)$$

Using this methodology, we have prepared a wide variety of $ZnS_6(N\text{-donor})_2$ 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 $ZnS_6(TMEDA)$ adopts a tetrahedral geometry with a seven-membered ZnS_6 ring [3].

Ligand competition studies on solutions of ZnS_6L_2 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 ($pK_a = 7.33$) and quinuclidine ($pK_a = 10.95$), but not by pyridine ($pK_a = 5.23$). On the other hand, the very labile pyridine analog, ZnS_6py_2, is a useful precursor to adducts of more specialized donors, such as TEEDA (N,N,N',N'-tetraethylethylenediamine) and (-)-sparteine, which can not be prepared by direct L/Zn/S_8 reactions. Crystallographic analysis of $ZnS_6\{(-)\text{-sparteine}\}$ indicates it to be a mixed-crystal complex best described as $[ZnS_6\{(-)\text{-sparteine}\}]_{0.8}[ZnS_5\{(-)\text{-sparteine}\}]_{0.2}$. 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^-. $ZnS_6(TMEDA)$ engages in conventional reactions with S_6^{2-} (to give ZnS_{12}^{2-}) and electrophilic acetylenes (to give the dithiolene complexes).

Solid $ZnS_6(TMEDA)$ 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:


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Submicron cubic ZnS is generated upon partial desulfurization of $ZnS_6(TMEDA)$ with tertiary phosphines (eq 2) as established by electron microscopic studies.

$$ZnS_6(TMEDA) + 5\ PBu_3 \longrightarrow ZnS + 5\ Bu_3PS + TMEDA \qquad\qquad (2)$$

The reaction of $ZnS_6(MeIm)_2$ with 5 equiv of zinc dust affords nanosize material $ZnS(MeIm)_{1\sim x}$ ($x \approx 0\ \text{-}\ 0.3$). Unlike cubic ZnS, this species is very reactive towards MeIm solutions of sulfur to afford $ZnS_6(MeIm)_2$. This result suggests that the nanosize material is an intermediate in the formation of $ZnS_6(MeIm)_2$ from the reaction of zinc, sulfur, and MeIm. Its formulation is supported by TGA, XPS, CL, and SS MAS ^{13}C NMR spectroscopic measurements. The $ZnS(MeIm)_{1\sim x}$ species also reacts with $Cu_4S_{10}(MeIm)_4$ [4c] to afford $[Zn(MeIm)_6][Cu_4S_{12}]$.

The species $ZnS_6(TMEDA)$ is a potent polysulfido-transfer reagent. The reaction of this zinc reagent with Cp_2TiCl_2 gives Cp_2TiS_5, which is a widely cited polysulfido-group transfer reagent itself [5]. Treatment of a CS_2 slurry of $ZnS_6(TMEDA)$ with Se_2Cl_2 gives 1,2-

Se_2S_6, as confirmed by reverse phase HPLC, Raman, and ^{77}Se NMR spectroscopic measurements (eq 3) [5].

$$+ \ ZnCl_2(TMEDA) \qquad (3)$$
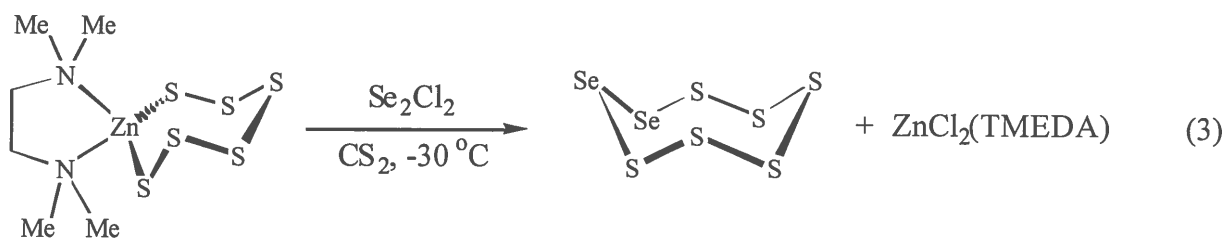
The reaction of CH_2Cl_2 solutions of $ZnS_6(TMEDA)$ with $TiCl_4$ affords a brown solid TiS_x (x~10). Unlike other titanium sulfides, this material is soluble in donor solvents. Extraction of TiS_x with MeIm affords the molecular complex $Ti(S_2)_2(MeIm)_3$, which can be considered a Lewis base adduct of $Ti(S_2)_2$. Crystallographic analysis reveals a pseudo trigonal-bipyramidal geometry around Ti, with the two of the MeIm ligands occupying axial sites. Solutions of $TiS_4(MeIm)_3$ are extremely sensitive to air. Oxygenation generates the dinuclear μ-oxo species $[Ti_2(S_2)_2(\mu\text{-}S_2)(\mu\text{-}O)(MeIm)_4]$, as confirmed by single crystal X-ray diffraction.

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