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Sulfur Transfer Reactions of a Zinc Tetrasulfanido Complex

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<u>Abstract</u>

A zinc tetrasulfanido complex supported by a bis(carboxamide)pyridine ligand framework has been synthesized by the insertion of elemental sulfur into the zinc–S(thiolate) bond of a zinc dithiolate complex ($[LZn]^{2-}$). This paper reports on sulfur transfer reactions of this polysulfanido complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions of metal polysulfido complexes. Complex ($[1]^{2-}$) and compares this behavior to known reactions ($[LZn]^{2-}$) and free elemental sulfur in solution. Although triphenylphosphine abstracts sulfur from ($[1]^{2-}$ to form ($[LZn]^{2-}$, complex ($[LZn]^{2-}$ can abstract sulfur from the zinc polysulfido complex (TMEDA)ZnS₆ (TMEDA = N,N,N',N'tetramethylethylenediamine). The tetrasulfanido complex ($[1]^{2-}$ can also transfer sulfur to dimethyl acetylenedicarboxylate to form a zinc dithiolene complex. These studies demonstrate that the zinc complex with a tetrasulfanido moiety can undergo similar reactions as metal complexes with purely inorganic polysulfido groups, although the final metal-containing products are different.

Introduction

Transition metal polysulfido complexes (L_nMS_x, Fig. 1 left) have been extensively studied as intermediates in the synthesis of metal sulfide materials and as structural analogs of biological active sites.¹⁻³ These compounds are typically synthesized by the addition of elemental sulfur or anionic polysulfides to a metal precursor, and examples with metals including titanium, nickel, copper, and zinc, among others, have been prepared and structurally characterized.⁴⁻⁷ The rearrangement of metal-bound polysulfido moieties is facile, permitting great diversity in the structure of such complexes.^{6,8,9} The reactivity of metal polysulfido complexes is also well

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explored. For example, metal polysulfido complexes have been shown to undergo catenation readily to form new polysulfido complexes.^{10,11} These species can also transfer sulfur atoms to chalcogens and phosphines, and perform nucleophilic attack on electron-poor alkenes and alkynes.^{4,12-15} Sulfur-atom abstraction from metal polysulfido complexes to form shorter-chain polysulfide moieties has also been demonstrated.¹³ Altogether, compounds in this class serve as useful precursors to a number of molecules and materials of fundamental interest.

Figure 1 compares the structure of polysulfido complexes with that of *polysulfanido* complexes, a class of compounds whose reactivity has been far less studied. Although there are numerous examples of metal persulfido complexes (persulfido = RSS⁻), there are few reported examples of complexes containing polysulfanido moieties ($R(S)_xS^-$, x > 1).¹⁶⁻¹⁸ While it is hypothesized that persulfides are more nucleophilic than their corresponding thiolates, the effect of additional sulfur atoms on nucleophilicity and sulfur transfer behavior is not well known.¹⁹ Nevertheless, the reactivity of metal polysulfanido complexes presents an interesting target of study, as these species may be relevant as models of species formed during biological sulfur redox signaling processes.¹⁹ Further, in comparison to metal polysulfido complexes, which can thermally degrade into species of higher nuclearity or to heterogeneous metal sulfide materials upon sulfur transfer,^{6,20} polysulfanido complexes may potentially act as reversible homogeneous sulfur transfer agents by regeneration of the metal thiolate precursor.



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∑^S_(S)_x ^S_R

R = alkyl, aryl

Polysulfido

Polysulfanido

Figure 1. Comparison of metal polysulfido and polysulfanido motifs.

Recently, we reported the synthesis of a zinc tetrasulfanido complex, $[1]^{2-}$, via the unusual insertion of three sulfur atoms into the Zn–S bond of zinc dithiolate complex, $[LZn]^{2-}$.²¹ Here, we report the sulfur transfer reactivity of $[1]^{2-}$. We demonstrate that the zinc dithiolate complex $[LZn]^{2-}$.

can abstract sulfur from a zinc polysulfido complex, but that the resulting tetrasulfanido complex is also in equilibrium with free elemental sulfur. We also show that [1]²⁻ can transfer sulfur to an electron-poor alkyne to form a zinc dithiolene complex. These reactions of [1]²⁻ are compared to known reactions of relevant metal polysulfido complexes to illustrate differences and similarities between these two classes of polysulfur-containing coordination compounds.

Results

Sulfur exchange

We first compared the zinc tetrasulfanido complex $[1]^{2-}$ to the previously reported (*N*,*N*,*N'*,*N*-tetramethylethylenediamine)zinc hexasulfido complex, (TMEDA)ZnS₆.⁶ An equimolar mixture of the dithiolate precursor $[LZn]^{2-}$ with (TMEDA)ZnS₆ in *d*₆-DMSO showed complete conversion to the tetrasulfanido complex $[1]^{2-}$ within minutes by ¹H NMR spectroscopy (Scheme 1). Although the fate of (TMEDA)ZnS₆ after sulfur transfer could not be determined by ¹H NMR spectroscopy, it is likely that insoluble ZnS is formed, as (TMEDA)ZnS₆ has been shown to decompose to ZnS upon heating.⁶ While it is probable that $[1]^{2-}$ also ultimately decomposes to form ZnS at elevated temperatures, a *d*₆-DMSO solution of $[1]^{2-}$ showed only slow conversion to other soluble zinc-containing complexes at 80 °C (*t*_{1/2} ~ 16 d).



Scheme 1. Sulfur transfer from (TMEDA)ZnS₆ to [LZn]²⁻.

Both polysulfido complexes and polysulfanido complexes are capable of transferring sulfur to sulfur atom acceptors such as electron-rich phosphines. We have previously reported that treatment of [1]^{2–} with 3 equivalents of triphenylphosphine regenerates [LZn]^{2–}, but that treatment with fewer than 3 equivalents of phosphine forms only a mixture of [1]^{2–} and [LZn]^{2–} rather than zinc polysulfanido complexes with contracted ring sizes.²¹ This sulfur redistribution suggests that

 $[1]^{2-}$ is in fast exchange with free elemental sulfur, as this behavior is similar to that of the solution dynamics of the *cyclo*-S₈ allotrope of elemental sulfur. Although treatment of S₈ with triphenylphosphine results in sulfur abstraction to form triphenylphosphine sulfide, S₈ remains the primary sulfur species in solution due to fast sulfur exchange.²²

Figure 2 compares the negative-ion electrospray mass spectra (ESI-MS) of $[1]^{2-}$ and of a mixture of $[1]^{2-}$ and ${}^{34}S_8$ (3 S-atom equivalents) in CH₃CN (5.0 × 10⁻⁶ M) after 2 h at room temperature. The spectrum of the mixture displays signals at higher *m/z* values consistent with statistical incorporation of ${}^{34}S$ atoms at three different positions in the tetrasulfanido moiety of $[1]^{2-}$. This sulfur scrambling supports the proposal that $[1]^{2-}$ is in exchange with free elemental sulfur and $[LZn]^{2-}$ in solution. However, as ${}^{34}S_8$ and ${}^{32}S_8$ scramble in acetonitrile on a similar timescale (EI-MS, see ESI),²³ we could not determine whether this exchange occurs one sulfur atom at a time (Scheme 2A,B) or if three sulfur atoms are extruded simultaneously (Scheme 2C).

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Figure 2. Negative-ion electrospray ionization mass spectra of $[1]^{2-}$ (top) and of $[1]^{2-}$ with added ${}^{34}S_8$ (3/8 equiv) in CH₃CN (middle). The bottom trace shows the isotopic distribution calculated for a statistical distribution of ${}^{32}S$ and ${}^{34}S$ within the tetrasulfanido moiety.



Scheme 2. Possible pathways for sulfur exchange in [1]^{2–}. (A) Insertion of sulfur to form a pentasulfanido intermediate. (B) Dissociation of one sulfur atom to form a trisulfanido intermediate. (C) Simultaneous loss of all sulfane sulfur atoms to form [LZn]^{2–}.

To further study sulfur exchange by $[1]^{2^-}$, the methoxy-substituted zinc dithiolate complex $[L_{OMe}Zn]^{2^-}$ was prepared (Scheme 3). The ¹H NMR spectra of a mixture of $[L_{OMe}Zn]^{2^-}$ and $[1]^{2^-}$ in d_6 -DMSO showed transfer of sulfur from $[1]^{2^-}$ to $[L_{OMe}Zn]^{2^-}$ to form $[LZn]^{2^-}$ within minutes of mixing. These data support the proposal that exchange of the tetrasulfanido complex $[1]^{2^-}$ with elemental sulfur and $[LZn]^{2^-}$ is fast at room temperature, although we cannot rule out an associative mechanism of sulfur transfer from $[1]^{2^-}$ to $[L_{OMe}Zn]^{2^-}$ in this reaction.



[L_{OMe}Zn]^{2_}

[1_{OMe}]^{2–}

Scheme 3. Sulfur exchange between $[1]^{2\text{-}}$ and methoxy-substituted zinc dithiolate complex $[L_{\text{OMe}}Zn]^{2\text{-}}.$

Alkylation and sulfur transfer to electrophiles

We next studied reactions of [1]²⁻ with electrophiles to compare the nucleophilicity of the tetrasulfanido moiety to that of previously studied metal polysulfido complexes and of the parent thiolate complex. Whereas treatment of metal polysulfides with alkyl halides typically results in

sulfur alkylation to form alkyl polysulfanes,²⁴ treatment of $[1]^{2-}$ with methyl iodide resulted in methylation only at the ligand thiolate sulfur sites, rather than at the tetrasulfanido sulfur atoms, to form the previously reported methylated complexes $[(L^{Me}Zn)_2]^{2-}$ and $L^{Me2}Zn$ (Scheme 4, see ESI).²¹ This result may suggest that the tetrasulfanido moiety of $[1]^{2-}$ is less nucleophilic than the thiolate functional group, resulting in selective thiolate methylation followed by loss of elemental sulfur. However, it is possible that selective thiolate methylation can occur, as governed by the Curtin-Hammett principle, if the zinc dithiolate complex $[LZn]^{2-}$ is more reactive toward methyl iodide than $[1]^{2-.25,26}$



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Scheme 4. Treatment of [1]²⁻ with one and two equivalents of methyl iodide to yield thioether complexes.

We next studied the reaction of $[1]^{2-}$ with dimethyl acetylenedicarboxylate (DMAD). Addition of DMAD (1.1 equiv) to a yellow d_6 -DMSO solution of $[Et_4N]_2[1]$ at room temperature immediately formed a red solution (Scheme 5). This new species, **A**, displays 11 aromatic ¹H NMR signals, indicating that the two ligand arms are inequivalent. Compound **A** converts over several hours at room temperature in solution to form a mixture of two species, $[2]^{2-}$ and $[3]^{2-}$. The ¹H NMR spectrum of complex $[2]^{2-}$ shows 6 aromatic signals, indicating that the two ligand arms are symmetric. The ¹H NMR spectrum of $[2]^{2-}$ does not display any signals between 3–4 ppm, suggesting that no DMAD-derived product is associated with the complex. Instead, a singlet at 3.49 ppm in d_6 -DMSO is observed for $[3]^{2-}$ that is not associated with any aromatic ligand-derived signals, leading to the assignment of $[3]^{2-}$ as a zinc bis(dithiolene) complex. This assignment was

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supported by observation of a signal at 476.8620 m/z by ESI-MS. Small amounts (ca. 7%) of previously-reported complexes associated with oxidation of [**1**]^{2–} were also observed in the ¹H NMR spectrum.²¹

Complexes $[2]^{2-}$ and $[3]^{2-}$ were isolated from DMSO by adding diethyl ether to the dark red reaction mixture until a red oil separated from solution. The red zinc bis(dithiolene) complex $[3]^{2-}$ was separated from this mixture by extraction with acetone, leaving behind complex $[2]^{2-}$ as a yellow solid. Figure 3 shows the solid-state structure of $[Et_4N]_2[2]$ characterized by single crystal X-ray diffraction (XRD) of crystals grown from vapor diffusion of diethyl ether into a CH₃CN solution of $[2]^{2-}$. Complex $[2]^{2-}$ is a chiral D_2 -symmetric pseudo-octahedral zinc complex coordinated by two pyridine(dicarboxamide) ligand frameworks connected by trisulfide linkages, with average S–S bond distances of 2.0520(10) Å. The Zn–N2 and Zn–N5 distances between the zinc center and pyridine nitrogen atoms of $[2]^{2-}$ are 2.064(2) and 2.066(2) Å, respectively, consistent with first-row M²⁺ metal-ligand distances reported for metal atoms bound to pyridine.²⁷ The bond distances between zinc and the amide nitrogen atoms of the ligand framework are longer (ca. 2.225(2) Å) than the bond distances between zinc and the pyridine nitrogen atoms, likely due to the high coordination number at zinc. The bond angles around the zinc center are distorted from octahedral symmetry due to ligand strain, resulting in N1–Zn–N3 and N4–Zn–N6 angles of 149.80(8)°.

The formation of $[2]^{2-}$ from **A** can be considered a zinc-templated formation of a macrocyclic ligand framework containing two trisulfide bridges. This structure is related to that of a previously reported bimetallic trisulfide complex that is formed upon oxidation of $[1]^{2-.21}$ The formation of such a polysulfanide-containing macrocyclic framework by this route is somewhat unusual, as previous examples of macrocylic polysulfanide ligands have been prepared only by addition of S_2Cl_2 or other related sulfur sources to the parent dithiol ligand.²⁸ However, treatment of the free ligand precursor H₄L with SCl₂ formed a trisulfide bridge between the two thiol moieties of a single

molecule of the bis(carboxamide)pyridine ligand precursor rather than between two molecules of H₄L (See ESI).

Figure 4 shows the solid-state structure of $[Et_4N]_2[3]$ characterized by XRD of crystals grown from vapor diffusion of diethyl ether into an acetone solution of $[3]^{2-}$, confirming the assignment as a dianionic pseudo-tetrahedral zinc bis(dithiolene) complex. The structure of $[3]^{2-}$ is consistent with previously reported structures of homoleptic zinc bis(dithiolene) complexes like bis(maleonitriledithiolato)zincate(II).²⁹ The long C–S bond distances of the dithiolene ligand (1.737(11)–1.7574(11) Å) are consistent with the fully reduced dithiolate form, as expected for the redox-inactive Zn²⁺ ion. The two dithiolene ligands coordinate to Zn²⁺ with near-tetrahedral geometry ($\tau = 0.68$).³⁰ The shortest Zn–S bond of $[3]^{2-}$ is 2.3098(4) Å and the longest is 2.3614(4) Å. In solution, complex $[3]^{2-}$ is dark red, with strongly absorbing bands at 364, 488, and 508 nm. The transition at 364 nm is assigned as a MLCT band based on studies of previouslycharacterized metal dithiolene complexes.^{31,32} We have not yet assigned the lower-energy transitions; although similarly intense low-energy bands have been observed in bis(dithiolene) donor-acceptor complexes³³ or assigned to interligand charge transfer,³⁴ complex $[3]^{2-}$ should not have similarly available acceptor orbitals.



Scheme 5. Reaction of [1]²⁻ with DMAD.

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Figure 3. Solid-state structure of [2]^{2–} as 50% thermal ellipsoids. Hydrogen atoms, solvent molecules, and tetraethylammonium counterions have been removed for clarity.



Figure 4. Solid-state structure of [**3**]^{2–} as 50% thermal ellipsoids. Hydrogen atoms and tetraethylammonium counterions removed for clarity.

This zinc bis(dithiolene) formation from tetrasulfanido complex $[1]^{2-}$ has so far only been observed for the very electron-poor DMAD substrate. A solution of $[1]^{2-}$ and diphenylacetylene in d_6 -DMSO at room temperature showed no conversion. Treatment of $[1]^{2-}$ with methyl propiolate formed a mixture of as-yet-unidentified species, possibly due to the formation of multiple regioisomers. Altogether, these results suggest that the sulfur transfer reactivity of polysulfanido complexes to electrophiles resembles that of previously studied polysulfido complexes.^{6,14,35-37}

Despite the slow conversion of intermediate **A** to complexes $[2]^{2-}$ and $[3]^{2-}$, we have not yet been able to grow X-ray quality crystals of **A** for structural characterization by XRD. ¹H NMR spectra collected of a d_6 -DMSO solution of $[1]^{2-}$ and DMAD (1.1 equiv) showed that the aromatic peaks assigned to **A** decay on the same timescale as an upfield signal at 3.79 ppm arising from the protons of a DMAD-derived methoxy group. Integration of the aromatic proton signals of **A** and the upfield signal at 3.79 ppm suggest that **A** is a species with an associated equivalent of DMAD.

We tested the hypothesis that the intermediate **A** may be a vinylzinc species formed by insertion of DMAD into the Zn–S(tetrasulfanido) bond, as previously observed for the titanium polysulfido complex $1,4-[C_5H_4CH_3)_2Ti]_2S_4$.³⁸ Attempts to trap a putative vinylzinc intermediate with methyl iodide or protonation with water did not result in products that could be identified as resulting from such an intermediate by ¹H NMR spectroscopy (See ESI). As a result, although we cannot rule out that the initial reaction of $[1]^{2-}$ with DMAD forms a vinylzinc intermediate, **A** is more likely a rearranged isomer of the initial DMAD insertion.

We next studied the rates of conversion of **A** to complexes $[2]^{2-}$ and $[3]^{2-}$. Figure 5 shows the electronic absorption spectra of a mixture of $[1]^{2-}$ and DMAD (1.1 equiv) in CH₃CN over 24 hours at room temperature. The first spectral time point, recorded 30 seconds after combining DMAD and $[1]^{2-}$, showed complete consumption of $[1]^{2-}$. A band at lower energy grows in over several hours due to the formation of $[3]^{2-}$. Spectral fitting of these data showed that the decay of **A** and formation of $[2]^{2-}$ and $[3]^{2-}$ are consistent with a rate law that is second-order in **A** (see ESI). Taken together, we propose that complex **A** is a monometallic species formed upon insertion of DMAD into the Zn–S(tetrasulfanido) bond followed by fast rearrangement of the resulting vinylzinc species. This formation of **A** is then followed by a slow bimolecular step that results in ligand exchange to form the homoleptic complexes $[2]^{2-}$ and $[3]^{2-}$.

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Figure 5. Electronic absorption spectra sampled over time after addition of DMAD (1 equiv) to $[1]^{2-}$ in CH₃CN (2.5 x 10⁻⁴ M). The black trace is the spectrum of $[1]^{2-}$, the blue trace is the first spectrum collected 30 s after DMAD addition, and the red trace is the final spectrum collected 24 h after DMAD addition.

Discussion

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The reactions of [1]²⁻ described above show that the sulfur exchange and redistribution behavior of the tetrasulfanido moiety is similar to that of some examples of previously characterized ligand-coordinated metal polysulfido complexes. Rauchfuss and co-workers have demonstrated that removal of one sulfur atom from (TMEDA)ZnS₆ in THF solution does not form the desulfurized product (TMEDA)ZnS₅, but rather a mixture of (TMEDA)ZnS₆ and ZnS.⁶ In acetonitrile, however, the polysulfido complexes (TMEDA)ZnS₅ and (TMEDA)ZnS₄ have been observed in solution.¹¹ Similarly, a mixture of S₈ and the tetrasulfido complex (PMDETA)ZnS₄. (PMDETA = *N*,*N*,*N'*,*N''*,*Pi*-pentamethyldiethylenetramine) is in equilibrium with (PMDETA)ZnS₅. We note, however, that not all metal polysulfido complexes undergo this dynamic sulfur redistribution process; in some cases, sulfur abstraction or addition results in the formation of kinetically stable, isolable, polysulfido complexes with different ring sizes.³⁸

Although the sulfur exchange dynamics are similar between the zinc tetrasulfanido and aminecoordinated zinc polysulfido complexes, the primary difference between these two classes of compounds is the reversibility of sulfur addition and removal. For both (TMEDA)ZnS₆ and (PMDETA)ZnS₄, removal of sulfur atoms via the addition of excess phosphines results in the decomposition of the complexes and dissociation of the amine ligands to form ZnS. In the case of [**1**]^{2–}, however, sulfur abstraction is completely reversible, as the only product is the dithiolate complex [LZn]^{2–}. As such, it may be possible to use polysulfanido complexes as catalytic sulfur transfer agents using elemental sulfur as the sulfur source.

The reactions of $[1]^{2-}$ with electrophiles suggest that the tetrasulfanido moiety may be less nucleophilic than the metal thiolate functional group, but these results remain inconclusive. The selectivity of methylation at the thiolate sulfur atoms supports the proposal that the zinc thiolate moiety is more reactive, but we cannot rule out the possibility of methylation at the tetrasulfanido group to form a methyl aryl tetrasulfide species followed by elimination of elemental sulfur. Additionally, while the analogous addition of dichloromethane to $[LZn]^{2-}$ results in chloromethylation of a thiolate sulfur (ESI-MS), addition of dichloromethane to $[1]^{2-}$ forms an intractable mixture of products. This divergent behavior suggests that the alkylation of the tetrasulfanido group is more complicated and electrophile-dependent.

The above reactions also show that complex $[1]^{2-}$ displays comparable nucleophilicity to that of the polysulfido complex (PMDETA)ZnS₄ and to the binary metal sulfides $[M(S_x)_2]^{2+}$ (M = Zn, Cd, Ni),³⁹ and greater nucleophilicity than the lower-coordinate (TMEDA)ZnS₆. As discussed above, the conversion of $[1]^{2-}$ to the putative DMAD insertion product **A** is complete within seconds at room temperature, similar to the reaction between (PMDETA)ZnS₄ and DMAD.¹¹ In contrast, the formation of (TMEDA)ZnS₂C₂(CO₂Me)₂ by addition of DMAD to (TMEDA)ZnS₆ requires several hours to reach completion.⁶

Conclusions

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From a purely compositional and structural perspective, a metal polysulfanido complex might be expected to exhibit properties related to both metal thiolate and metal polysulfido complexes. The experiments discussed above support this assumption. We have shown that the zinc

tetrasulfanido complex [1]²⁻ undergoes reactions similar to amine-coordinated zinc polysulfido complexes, including sulfur exchange and sulfur transfer to the electron-poor alkyne dimethyl acetylenedicarboxylate. Current studies are underway to elucidate additional factors governing polysulfanido reactivity; we anticipate that, as with metal polysulfido complexes, modification of the ancillary ligand framework will permit isolation of new polysulfanido complexes with distinctive sulfur dynamics or nucleophilicity.

[†]Electronic supplementary information (ESI) available. Synthetic procedures, compound characterization, crystallographic data. CCDC 1996091 and 1996092.

Conflicts of Interest

There are no conflicts to declare.

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The sulfur transfer reactions of a zinc tetrasulfanido complex are explored and contrasted with those of metal polysulfidos.