Structural and Redox Interconversions of Sulfur Ligands of Transition Metal Complexes

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The interactions between transition metals and sulfur have long been studied for potential applications in catalysis and energy storage and due to the relevance of these motifs in biological and geological systems. Complexes with sulfur-containing ligands can undergo redox transformations centered on sulfur as well as at the metal. Sulfur also readily catenates with other sulfur centers to form polysulfur motifs. Here, the synthesis and structures of notable examples of metal complexes with sulfur-containing ligands (sulfido, polysulfido, and polysulfanido) are described. Aspects of sulfur-centered redox, including spectroscopic and structural considerations, and future research opportunities are highlighted.

Keywords: transition metals; sulfur; redox

1. Introduction

Interactions between transition metals and sulfur in Nature are common, serving both structural and functional roles. These motifs are found in heterogeneous materials like metal sulfide minerals and in sulfur-containing metalloenzymes with coordinating cysteine or other residues. This connection has given rise to proposals that biological iron-sulfur clusters arose from bacterial incorporation of surrounding iron sulfide minerals.[1-2] Sulfur-centered reactions at coordinating thiolates and at metal-bound H_2S, HS^-, or S^{2-} ligands are common for metalloenzymes and metallocofactors in biological systems. Figure 1 shows selected examples of metal centers in biology that display sulfur-centered redox chemistry. For example, hydrosulfide oxidation at heme centers in hemoglobin, myoglobin, and cytochrome *c* oxidase form thiosulfate and hydropolysulfides,[3-4] and can also participate in sulfur transfer to other substrates or to the porphyrin itself.[5] Persulfide species have also been shown to play a role in the self-assembly of multimetallic sites like Fe_4S_4 clusters,[6] or at structural zinc finger

proteins.[7] Metal-sulfur-containing compounds are also commonly used in industrial applications ranging from petroleum hydrodesulfurization to photovoltaic energy conversion.[8-9] For these reasons, the rational synthesis of compounds containing metal-sulfur interactions to model these structures and understand their fundamental reaction mechanisms has been an ongoing area of research for the past century.

In transition metal-sulfur compounds, chemistry at the sulfur center often contributes heavily to the properties and reactivity of the compounds, in some cases as much as the metal center itself. Reduced sulfur species such as sulfide anions also exhibit relatively positive electrochemical potentials, meaning that they are readily oxidized ($E^o(S/S^{2-}) = -0.447$ V vs. NHE).[10] As a result, sulfur-centered redox processes can occur at similar potentials as metal-centered redox. Compared to oxygen, sulfur is both larger and "softer," and M–S bonds can display high degrees of covalency.[11] From a structural perspective, the large and diffuse 3*p* orbitals of sulfur form weaker π-interactions with metal centers or with other atoms, meaning that sulfur tends to form bridging rather than terminal interactions with transition metals. Between sulfur centers, catenation and formation of S–S bonds commonly results in polysulfur products, for example in the abundant cyclo-S_8 allotrope of elemental sulfur or in anionic polysulfides, in which sulfide (S^{2-}) is catenated by other, formally S^0, sulfur atoms.[12-15] Polysulfur compounds are also often dynamic in solution, resulting from exchange between species with different polysulfur chain lengths.[13]

Interactions between neighboring sulfur centers can dramatically change the properties of polysulfur-containing species due to inductive effects and lone pair-lone pair repulsion. For example, perthiol compounds (RSSH, R = aryl or alkyl) are more reducing than the corresponding thiols (RSH). Where RSH is a cysteine moiety with $pK_a \sim 8.8$, $E^o(RSS^{\cdot}/RSS^{-}) = 0.68$ V and $E^o(RS^{\cdot}, H^+/RSH) = 0.96$ V vs. NHE.[16] This

sulfur-sulfur interaction also changes the reactivity at the terminal sulfur center – perthiols have been estimated to be more acidic than the parent thiol by two to four pK_a units, depending on the substituent.[17-19] Deprotonated persulfide anions have also been proposed to exhibit the α-effect, that is, that heteroatoms adjacent to the nucleophilic moiety result in higher nucleophilicity than expected due to lone pair-lone pair repulsion.[17-18] However, this effect is well established only for 2*p* elements, and such effects for 3*p* elements like sulfur are controversial.[20] Polysulfur-containing compounds can be electrophilic as well, reacting with nucleophiles to cleave the S–S bond and release sulfide or thiolate anions. Polysulfur-containing compounds are also prone to disproportionation, releasing sulfur in the form of S_8 and yielding shorter polysulfur analogs. Due to this rich sulfur-centered chemistry, transition metal-sulfur chemistry is very diverse, and understanding the formation, interconversion, and subsequent reactivity of sulfur or polysulfur ligands remains highly relevant.

The purpose of this Comment is to discuss trends in the coordination chemistry and sulfur reactivity of synthetic transition metal complexes with sulfido or polysulfur-containing ligands. Figure 2 shows the scope and organization of the review, as well as the nomenclature that will be commonly used throughout. First, reagents and methods relevant to the synthesis of these compounds will be presented. Second, salient examples of transition metal complexes of all-inorganic sulfido (S^{2-}) and polysulfido (S_x^{2-}) will be mentioned. Third, examples of polysulfanido complexes (metal complexes with RS_x^- ligands, R = alkyl, aryl, etc.) will be discussed. In each section, synthetic strategies and important examples will be noted, as well as further discussion of salient structural and electronic characteristics, including redox properties, structural interconversion, and further reactivity, with particular attention to the sulfur-centered

chemistry. Last, we will discuss the relevance of these species toward broader areas of study as well as ongoing synthetic targets and opportunities in the field.

2. Metal Hydrosulfide, Sulfido, and Polysulfido Compounds

2.1. Synthesis of Transition Metal Sulfido and Hydrosulfido Complexes

Scheme 1 shows general synthetic strategies for metal sulfido or hydrosulfido complexes. Broadly speaking, metal-sulfido motifs can be prepared by addition of sulfur as sulfide (S^{2-}, Scheme 1A) or by the reductive addition of elemental sulfur (S_8, Scheme 1B).

Gaseous H_2S is a commonly used reagent and can form M–S bonds by protonolysis of basic transition metal species like metal alkyls, hydrides, hydroxides, or alkoxides (for H_2S, pK_1 6.98, pK_2 > 17 at 25 °C in H_2O).[19] H_2S can be purchased commercially in lecture bottles or gas cylinders, or can be generated by the addition of acid to sulfide salts.[21] H_2S has an unpleasant odor and is toxic in high concentrations, and should be handled only in fume hoods and quenched using aqueous zinc solutions to form ZnS.[22] Sulfide and hydrosulfide salts can be used as alternative, non-volatile sulfide sources (Scheme 1A). While alkali salts such as NaHS and Na_2S are minimally soluble in organic solvents, the more soluble tetrabutylammonium hydrosulfide (Bu_4NSH) reagent can be prepared for use instead.[23]

Other sulfide synthons form M–S bonds from M–O bond-containing precursors promoted by the driving force for formation of more stable oxygen-containing byproducts (e.g. $(Me_3Si)_2O$, triarylphosphine oxide, etc.).[24-27] The thermodynamics of sulfur transfer have been broadly reviewed for other reagents.[27]

Bis(trimethylsilyl)sulfide [$(Me_3Si)_2S$] is a commonly used sulfur transfer reagent in both organic and organometallic chemistry,[28] and has also been used in the synthesis of

metal sulfide nanomaterials.[29-31] Other commonly used reagents include Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-dithione), B_2S_3, CS_2, and thiocarbamates.

More oxidized sulfur sources have also been used to form metal sulfido species, but typically require reduction prior to M–S bond formation (Scheme 1B). Elemental sulfur is an attractive feedstock due to its abundance and low cost. S_8 is stable to air and moisture, non-volatile, and can be readily purified by sublimation or by recrystallization from hot toluene. However, the low solubility of S_8 in both water (4.9 μg L^{-1} at 25°C) and organic solvents can present a disadvantage.[32-34] For the addition of small quantities of S_8 in organic solvents, a stock solution in toluene (ca. 10 mg/mL) can be prepared. Outside of synthetic applications (e.g. in biochemical studies), encapsulating compounds (e.g. cyclodextrins or cucurbiturils) or charged surfactants have been employed to increase the solubility of S_8 in water.[35-37] Alternatively, it is possible to prepare polysulfide anions ($S_3^{\bullet -}$ and S_x^{2-}, x = 5 in aqueous solution, 4 & 6 in THF) upon addition of sulfide to S_8 or by reduction of S_8 using external reductants or bases.[38-39] These species exchange readily in solution, but can also act as soluble sources of S^0.[13, 40] Polysulfide anions are readily oxidized and should be handled under inert atmosphere.

Other sulfur transfer reagents rely on weak S–S or C–S bonds that are readily cleaved. For example, benzyl trisulfide has been used as a soluble S^0 source that releases dibenzyl disulfide as a byproduct.[41] Thiiranes like propylene sulfide or styrene sulfide have also been used to transfer sulfur and extrude the corresponding alkene.[27] In some cases, cleavage of thiol or thiolate C–S bonds for sulfur transfer can also occur; this can proceed under mild conditions[42-43] and is also commonly used at high temperatures in the synthesis of metal sulfide nanomaterials.[44-45] Other M–S, S–S, and

C–S bonds can be formed by the addition of nucleophilic species to electrophilic sulfur precursors. For example, phthalimido compounds containing weak N—S bonds have been shown to transfer RS^+ fragments with concomitant phthalimide protonation or metal coordination.[46-47] Sulfur halides like SCl_2 and S_2Cl_2 are also commercially available or can be readily prepared for use as S^{2+} or S_2^{2+} synthons.[48]

Transition metal sulfido and polysulfido complexes are typically characterized structurally using standard methods used for organometallic and coordination compounds like ^{1}H NMR spectroscopy and single crystal X-ray diffraction (XRD). The latter method is of primary use in measuring M–S and S–S bond distances and characterizing π-bonding interactions. While ^{33}S is spin-active (I = 3/2), it is of low abundance and low sensitivity, and is not typically employed in characterizing these compounds.[49] X-ray absorption spectroscopy (XAS) methods have been primarily used to study the covalency of M–S bonds in proteins,[11] but have also been applied to synthetic compounds.

The vibrational spectroscopy of terminal metal sulfido complexes show stretching vibrations ν(MS) in characteristic regions (400-500 cm^{-1}), but the low energies of these bands are therefore of less diagnostic use than those of the corresponding metal oxo complexes, which occur at slightly higher energies (800-1000 cm^{-1}).[50] The vibrations of sulfur-sulfur bonds in organic disulfide compounds show characteristic Raman signals at ν(SS) ~ 500 cm^{-1}.[51-52] The spectra of S_8 and the polysulfide anions have also been measured.[52-53] The use of these energies in conjunction with isotopic labeling and computation can provide information about structure and bonding within these compounds.

Many transition metal sulfides are highly colored with intense ligand-to-metal charge transfer (LMCT) bands, which are often low in energy due to the readily

oxidizable sulfur centers. Polysulfide anions themselves can be highly colored; the trisulfur radical anion ($S_3^{\cdot -}$) is an intense blue color, while dimerization to the S_6^{2-} dianion becomes intensely red.[54] In aqueous solution, other polysulfide anions tend to be yellow.[13]

2.2. Transition Metal Hydrosulfido and Sulfido Complexes

Figure 3 shows the coordination modes of the hydrosulfide (HS^-) ligand, which can exhibit both terminal[55-57] and bridging (μ_2- and μ_3-) coordination modes. Synthetic transition metal hydrosulfido complexes have been prepared as models of biological metal hydrosulfido species and also as intermediates toward the synthesis of transition metal sulfido complexes. Pluth and Tonzetich have comprehensively reviewed synthetic examples of recently reported transition metal hydrosulfido complexes,[58-59] and this section will focus the discussion upon sulfur-centered reactivity.

As biological Zn^{2+} centers commonly display four-coordinate, tetrahedral geometries with N_xS_{4-x} binding motifs, tris(pyrazolyl)borate ligands and their derivatives have been used to model these systems.[60] Scheme 2 shows examples of reactions of tris(pyrazolyl)borate-supported zinc hydrosulfido complexes (**1**-**4**). In most cases, the hydrosulfide ligand acts as a typical nucleophilic base. For example, protonolysis of the hydrosulfide ligand with a thiol (R′SH, R′ = 4-$NO_2C_6H_4$, Et, ^{i}Pr, Bn, 2-EtSH, 3-PrSH) or oxygenic acid (2,4,6-trinitrophenol, benzoic acid, phenylacetic acid, hexafluoroacetylacetone) releases H_2S and forms the corresponding zinc thiolate, alkoxide, or carboxylate complexes. The hydrosulfide moiety can also be alkylated by treatment with methyl iodide to form CH_3SH and the corresponding zinc iodide complex.

The hydrosulfide ligand can also act as a Brønsted acid. Zinc hydrosulfido species **1**-**4** can be deprotonated to form heterogeneous ZnS and free

tris(pyrazolyl)borate ligand. Deprotonation of other transition metal hydrosulfido complexes results in the formation of sulfido-bridged molecular species. Scheme 3 shows an example in which the di(hydrosulfido) complex $Cp_2Zr(SH)_2$ (**5**) is deprotonated to form a bimetallic bridged-sulfido complex, $[Cp_2Zr(\mu_2\text{-}S)]_2$ (**6**).[61] Other multimetallic bridged-sulfido clusters form by self-assembly upon addition of other sulfide-transfer reagents.

As with transition metal hydrosulfido complexes, transition metal sulfido complexes have been extensively reviewed,[8] and only select examples will be discussed below. Sulfido ligands can bridge between two and four metal centers and have been shown to enhance electronic communication between the metal centers. Compared to analogous bridging oxo motifs, the more diffuse orbitals of sulfur are proposed to effect greater charge distribution and subsequently better magnetic exchange between metal centers.[62-63] Sulfide ligands have also been considered to play functional roles, for example as sites of protonation during N_2 reduction by the FeMo cofactor of nitrogenase.[64] More recently, a μ_4-sulfido ligand of a synthetic [4Cu:1S] model of N_2O reductase (**7**) has been proposed to act as a participating site in N_2O reduction, based on computational and XAS studies (Figure 4).[65] This additional reactivity is proposed to be facilitated by the high degree of covalency between Cu and S in this complex.

The isolability and stability of less common *terminal* metal sulfido complexes are dictated by occupation of M– S π* orbitals in a similar fashion as terminal metal oxido complexes. Figure 5 shows the molecular orbital diagram of a terminal metal sulfido complex with tetragonal geometry. As predicted by this orbital diagram, terminal sulfido ligands are commonly observed for electron-deficient (d^0–d^2) complexes, which permits M–S π-bonding interactions.[9] These π-bonding interactions

have been assigned primarily based on the shorter M–S bonds measured by XRD as well as based on DFT calculations.[24, 66-68]

Although there are relatively few examples of transition metal sulfido complexes with group III and IV metals, Bergman and co-workers prepared and structurally characterized a d^0 zirconium(IV) complex, $Cp^*_2Zr{=}S(L)$ (**9**, L = py) by deprotonation of the corresponding hydrosulfide complex $Cp^*_2Zr(SH)I$, followed by trapping of the [$Cp^*_2Zr{=}S$] intermediate using pyridine or other Lewis bases (Scheme 4).[69] The solid-state bond lengths measured by single crystal XRD indicate Zr−S π-bonding [d(Zr−S) = 2.316Å, while Zr–S single bonds range from 2.42–2.5 Å]. The analogous $Cp^*_2Ti{=}S(L)$ complex has also been isolated.[70] The terminal sulfido ligands of **10** are nucleophilic and can add to unsaturated substrates like 3-hexyne or benzonitrile to form sulfur-containing metallacycle products.[69]

There are many examples of terminal sulfido complexes of the transition metals from groups V-VII, particularly for V, Mo, W, and Re. The homoleptic thiometalate anions like MoS_4^{2-}, WS_4^{2-}, and ReS_4^- are common, readily prepared, and in many cases commercially available (Figure 6 left).[50, 71-72] Additional mixed thiometallate anions $MO_xS_{4-x}^{n-}$ have also been prepared. Heteroleptic variants of these complexes with ancillary supporting ligands have been isolated and structurally characterized. For example, Enemark and Young prepared sulfidomolybdenum(IV) complexes supported by tris(pyrazolyl)borate ligands (Figure 6 right, **11**).[73] These complexes are readily prepared by conversion of the corresponding oxometallate anions to the thiometallate derivative by replacement of oxygen for sulfur by treatment with H_2S in the presence of base or by addition of bis(trimethylsilyl)sulfide and formation of hexamethyldisiloxane. Alternatively, Parkin and co-workers synthesized d^2 $L_4W(S)_2$ complexes (L = PMe_3, CNR [R = ^{i}Pr, ^{t}Bu, cyclohexyl]) by deprotonation of H_2S by a W(IV) tetrahydrido

precursor.[74] In many cases, the final sulfido-containing complexes are more highly colored than the oxido or hydrido precursors due to intense S→M charge transfer bands, permitting monitoring of reaction progress using electronic absorption spectroscopy.

Due to the π-bonding characteristics of these complexes, terminal sulfido ligands can act as both nucleophiles and electrophiles. As an example of the former pathway, Rauchfuss and co-workers demonstrated that the tetrathioperrhenate anion reversibly forms metallacycle adducts with alkenes (Scheme 5).[75-78] A similar reaction has been demonstrated with WSe_4^{2-} and electron-poor alkynes like dimethyl acetylenedicarboxylate (DMAD).[79] As an example of electrophilic reactivity, MoO_3S^{2-} and $MoO_2S_2^{2-}$ react with cyanide to form SCN^- as well as cyano complexes of reduced molybdenum.[80]

There are fewer examples of terminal metal sulfido complexes of the later transition metals, due to population of M−S π* orbitals. Hayton has recently reviewed these complexes and only a brief overview is presented here.[81] Phosphine-supported nickel sulfido complexes have been transiently formed by thermolysis and deprotonation of a hydrosulfide precursor complex.[82-83] Figure 7 shows examples of isolated and structurally characterized late transition metal terminal sulfido compounds. In each of these examples, the sulfide moiety is further stabilized, whether through hydrogen-bonding interactions with the supporting ligand framework (M = Fe, **13**)[84] or by stabilizing interactions with a nearby Lewis acid (e.g. $[K(18\text{-crown-6})]^+$ and $[K(2,2,2\text{-cryptand})]^+$, M = Ni and Zn, **15** and **16**, respectively).[42, 85] Due to the scarcity of these examples, the sulfur reactivity of these species has been far less explored.

2.3. Transition Metal Polysulfido Complexes

Transition metal polysulfido complexes are related to metal sulfido complexes by the catenation of additional formally "S^0" centers to the sulfide center. These S_x^{2-} ligands (x = 4–9) typically form chelates to a single metal center, although bimetallic bridged examples have also been isolated.[86] Polysulfido complexes of metals spanning the *d* block have been isolated and structurally characterized. These complexes have been reviewed by Rauchfuss and others.[87-88] Figure 8 shows some selected examples.

Homoleptic chiral late transition metal complexes of Pt with all-inorganic polysulfide ligands have been prepared by treatment of the corresponding metal halide salt with polysulfide solutions generated by addition of sulfide to S_8 (Fig. 8, **17**).[89-90] Coucouvanis and co-workers synthesized a series of all-inorganic metal polysulfide compounds (M = Mn, Ni, Zn) by the addition of dibenzyl trisulfide to the corresponding metal thiolate salts.[91] Interestingly, despite the similarity between these complexes, the structures exhibit a range of different polysulfide lengths (Fig. 8). For example, the nickel congener (**18**) is coordinated by two S_4^{2-} ligands, while the manganese congener (**19**) displays both a S_6^{2-} chelate as well as an S_5^{2-} chelate.

Heteroleptic transition metal polysulfido complexes with supporting ligands have also been prepared. The titanocene pentasulfide complex, Cp_2TiS_5 (**20**) was first prepared by addition of S_8 to $Cp_2Ti(CO)_2$ and has also been prepared by the addition of polysulfide anions to Cp_2TiCl_2. Rauchfuss and co-workers pioneered a synthesis of zinc polysulfide complexes by the in situ reduction of sulfur to polysulfide anions by Zn^0 in the presence of amine donors.[92] In these systems, the supporting amine ligand influences both the polysulfide chelate ring size as well as sulfur reactivity (**21** and **22**).[93] These compounds are capable of transfer of polysulfide moieties or S^{2-} to various substrates, including to $SeCl_2$,[94] CS_2, and electron-poor alkynes.[93]

Transition metal sulfido and polysulfido can interconvert by the addition of "S^0" equivalents or by sulfide oxidation, particularly when sulfur oxidation occurs at similar potentials as metal-centered redox. For example, oxidation of MoS_4^{2-} (e.g. by addition of an organic disulfide) results in the oxidation of the sulfides to disulfido anions (S_2^{2-}) and forms a bimetallic $[Mo_2S_8]^{2-}$ species **23** (Scheme 6). Addition of S_8 to MoS_4^{2-} results in the formation of coordinated S_4^{2-} polysulfide ions and reduction of Mo^{VI} to Mo^{IV} (**24**).

Other examples of sulfido/polysulfido interconversion have been demonstrated with transition metal centers whose redox potentials are less accessible than those of sulfur (or with redox-inactive metal ions). Scheme 7 shows the oxidation of a sulfido-bridged yttrium cluster (**25**) by the addition of S_8 to form bimetallic η^2-disulfido-bridged complexes (**26**). Further addition of S_8 forms a monomeric yttrium pentasulfido complex (**27**).[95] This intriguing example therefore demontrates *stepwise* sulfur-centered interconversion by the addition of controlled amounts of S_8. This final pentasulfido moiety is nucleophilic and can transfer sulfur to alkyl-substituted silyl chloride reagents or to alkyl halide compounds.

The reverse process (metal polysulfido reduction) can also occur. Pluth and co-workers have recently demonstrated that a tris(pyrazolyl)borate-supported molybdenum tetrasulfido complex can undergo nucleophilic attack by hydrosulfide, resulting in hydrosulfide oxidation and formation of a molybdenum center with three terminal sulfido moieties.[96] The η^2-disulfido complex $Cp^*_2Ti(S_2)$ (**28**) has also been shown to undergo sulfur-centered reduction to form $Cp^*_2Ti(SH)_2$ (**29**) upon treatment with H_2 (Scheme 8).[97] In short, hydrosulfido, sulfido, and polysulfido complexes can be reversibly interconverted.

Disulfido ligands in particular display interesting redox activity. The diphosphine-supported nickel disulfido complex (**30**) was oxidized to release S_8 and bridge to a second nickel center (Scheme 9). A related N-heterocyclic-carbene-supportd disulfido-bridged dinickel complex was also shown to undergo reduction to form the di(μ_2-sulfido) dinickel complex.[98] Recent structural, spectroscopic, and computational work by Berry and co-workers have demonstrated that disulfido ligands can, in some cases, coordinate as the "subsulfido" ligand (S_2^{3-}), which exhibits a S–S half-bond.[99] A survey of existing complexes showed that the oxidation states of transition metal-bound disulfido and diselenido (E_2) units are quantized, ranging from 2 E^{2-}, E_2^{3-}, and E_2^{2-}, and not a continuous progression of E−E bond orders. We note, however, that this type of "half-bond" interaction is limited to disulfido (or other dichalcogenido) ligands, and does not extend to longer polysulfido chains that do not exhibit η^2 coordination motifs.

As shown above, a principal difference between sulfido and oxido ligands in these complexes is the accessibility of structures with $[S_x]^{2-}$ ligands where $x > 2$. Questions regarding redox and steric control over polysulfur speciation and reactivity in these polysulfide complexes remain challenges, however. For chelate structures, the polysulfide ring size appears to be thermodynamically controlled, and kinetic access to other ring sizes has not been demonstrated.

3. Metal Polysulfanido Complexes

3.1. Synthesis of Metal Disulfanido Complexes

Polysulfanido anions are thiolate anions with S^0 centers catenated to the thiolate sulfur center (RS_x^-, R = alkyl or aryl, $x > 2$). The majority of characterized transition metal polysulfanido complexes are disulfanido complexes ([M]SSR, where R= alkyl or aryl). These species have been accessed by a variety of synthetic routes, as shown in

Scheme 10. These methods can be broadly characterized as 1) C–S, 2) S–S, and 3) M–S bond-forming reactions, or as 4) sulfur insertion reactions, in which multiple types of bonds are formed.

Metal polysulfanido species have been generated by the formation of C–S bonds upon nucleophilic alkylation of metal polysulfido complexes (Scheme 10a). For example, molybdenum, manganese, and nickel polysulfide chelates (**34, 18**, **19**) were shown to perform nucleophilic attack on carbon disulfide to form the tetrathiocarbonate species (**32**, **33**, **35**, Scheme 11).[91, 100-101] It is notable that these reactions are selective for five-membered chelate products—the tetrasulfido moiety *loses* two sulfane atom equivalents during the nucleophilic addition reaction, suggesting the stability of the resulting five-membered ring exceeds that of other products with more sulfur atoms. Although polysulfido ligands are known to be electrophilic, metal polysulfanido synthesis through this route has not yet been demonstrated.

Polysulfanide moieties can also be generated by the formation of new S–S bonds (Scheme 10b). For example, treatment of a metal hydrosulfido complex by a "RS^+" synthon such as a *N*-thiophthalimide compound can be used to form the corresponding metal polysulfanido complex (Schemes 20 and 21, vide infra).[102-104] Scheme 12 shows an alternate example, in which a ruthenium-bound thiosulfonate ligand (**36**) undergoes nucleophilic attack by an organic thiolate.[105] In contrast with previous studies suggesting sulfur nucleophiles do not attack the S−S bond of metal thiosulfonates and instead favor ligand exchange similar to the above zinc example, this attack favors the proximal sulfur atom, forming the ruthenium disulfanido (**37**) with the release of phenylsulfinate. This unique reactivity was attributed to the slow substitution of ruthenium-bound sulfur ligands combined with the presence of good leaving groups.

As a third route, metal polysulfanido compounds can be generated by the formation of M–S bonds (Schemes 10c and 10d). For example, diphenyl trisulfide or *N*-(phenyldithio)phthalimide can oxidatively add across a titanium center in $Cp_2Ti(CO)_2$ (Scheme 13).[104] This reaction mirrors that of organodisulfide oxidative addition to form metal dithiolate complexes.[106-108] Interestingly, the reaction with diphenyl trisulfide breaks an S–S bond to form two Ti–S bonds (**39**) while the phthalimide-terminated reagent undergoes oxidative cleavage of the N–S bond (**38**).

As metal polysulfido complexes have been prepared by the addition of polysulfide anions to metal precursors, it should in principle be possible to synthesize metal polysulfanido complexes by the addition of the corresponding organo-substituted hydropolysulfide or polysulfanide anions (Scheme 10d). Perthiols or hydropolysulfides can protonolyze basic metal precursors (e.g. metal hydroxides) to form the resulting M–S bond.[109] Artaud and co-workers demonstrated that treatment of substituted tris(pyrazolyl)borate zinc hydroxide complexes with independently synthesized perthiols (RSSH, R = Ph_3C or ^{t}Bu) formed the corresponding zinc disulfanido species (**40**, **41**, Scheme 14).[109] Product isolation relies on the greater stability toward exchange of the protonated organic perthiol compound compared to the deprotonated disulfanide anions. Conversion of **40** or **41** to the corresponding metal hydrosulfido complexes is possible via reduction by deprotonated thiol, forming an organic disulfide compound and releasing free thiol. This complex was also shown to reversibly interconvert to a zinc thiolate complex upon treatment with the corresponding thiol in an initial ligand exchange step rather than thiolate attack on the S−S bond.

We note that the formation of metal polysulfanido complexes by addition of *polysulfanide* anions has not yet been demonstrated. Free polysulfanide anions have been synthesized by treatment of thiolate anions with elemental sulfur or other S^0

donors[110-114] and examples of phenyl- and *tert*-butyl-substituted disulfanide and tetrasulfanide anions with organic countercations (Et_4N^+, PPh_4^+, and PNP^+, PNP = bis(triphenylphosphine)iminium) or with transition metal cations have been isolated and structurally characterized by XRD, in some cases by fractional crystallization.[115-116] While these studies demonstrate that polysulfanide anions can be stable in the solid state, the same polysulfanide anions of different sulfur chain lengths have been demonstrated to exchange rapidly in solution. Due to this dynamic solution-phase behavior, it is likely that addition of these anions to metal halides or other related precursors would form a mixture of products.

Last, metal polysulfanido complexes can be formed via insertion of elemental sulfur (S_8) into either a metal-carbon bond to simultaneously form M–S and S–C bonds (Scheme 10e) or into a M–S(thiolate) bond to form new M–S and S–S bonds (Scheme 10f). We note that the insertion of sulfur into metal hydride bonds to form the corresponding hydrosulfido compound has been demonstrated for a platinum hydride complex.[56] This particular reaction appears to be more facile than that of insertion into the metal-carbon bond; the Pt-methyl moiety in the same molecule does not insert sulfur. Energetic factors governing this insertion have been previously published,[117] and other considerations will be further discussed below.

Early examples of the above approaches have been demonstrated for complexes containing M-S_x-SR motifs, specifically those containing dithiocarboxylate or trithiocarbonate ligands. Fackler and co-workers showed that elemental sulfur can insert into the M-S bond of dithiocarboxylate- or trithiocarbonate-supported nickel or zinc complexes to form the oxidized trithiocarboxylate ligand (**43**, **44**, Scheme 15).[118-119] We note that Scheme 15 shows the insertion of "S^0" between the dithiocarboxylate ligand and the metal center for simplicity. However, isotopic labelling of added sulfur

during these studies revealed that the mechanism is more complex and that labelled sulfur is incorporated into other positions of the resulting trithiocarboxylate ligand.

Insertion of more than one sulfur atom into a metal-carbon bond to form a disulfanide complex in an intriguing stepwise fashion was demonstrated by Legzdins and Sanchez.[120] In this reaction, an initial sulfur atom insertion into a W–CH_2SiMe_3 bond formed a tungsten thiolate moiety, followed by a second sulfur atom insertion step to form an η^2-disulfanide ligand. This second sulfur atom was observed to slowly migrate into another tungsten-carbon bond to form the final tungsten dithiolate complex. A later report by Ji and co-workers proposed that a stable ruthenium disulfanido complex was formed by migratory insertion of two sulfur atoms into the Ru—C bond of a diruthenium complex featuring a tetramethylfulvene ligand.[121]

A number of disulfanido-bridged bimetallic complexes and multimetallic clusters have been reported with structural characterization. Unlike bridging disulfido moieties, which can bind through both sulfur atoms in end-on or side-on fashions to the metal centers, disulfanido ligands bridge solely at the terminal sulfur center. These complexes have been synthesized by similar methods as discussed above, such as thiolate attack on bridging disulfides[122-124] or sulfur insertion into M–(μ-S) bonds.[125-128] In one example, $Fe_2(S_2)(CO)_6$ was observed to insert thiobenzophenone upon UV irradiation, resulting in the bridging alkyl disulfanido complex (**45**, Scheme 16).[129]

Many bridging disulfanido complexes are formed by self-assembly upon addition of CS_2,[130-131] RCS_2^- (e.g. dithiocarbamates, dithiocarbonates),[132-134] or similar reagents to various metal precursors, including metal sulfides and carbonyls.[135-137] Because of the required C−S bond cleavage of one ligand equivalent to convert another equivalent to a disulfanide, these syntheses often require heat and/or extended reaction times and result in lower (10-20%) yields. In the synthesis of a tetracopper

cluster bridged by trithiocarboxylates,[133] C−S bond cleavage of dithiocarboxylate was proposed to result in copper-mediated formation of thiocarboxylate in the presence of water, along with reduction of Cu^{2+} to Cu^{+} (**46**, Scheme 17).

3.2. Higher Order Metal Polysulfanido Complexes (MS_xR, x > 2)

There are fewer examples of structurally characterized metal polysulfanido complexes with longer polysulfur moieties. In one example, refluxing a xylenes solution of Cp_2TiS_5 (**20**) results in thermal rearrangement and nucleophilic attack upon the Cp ligand by the pentasulfide moiety (Scheme 18).[138] Proposed to be initiated by the short C−S distance between one of the Cp carbon atoms and the β-position sulfur atom in the solid state, three sulfur atoms migrate to dearomatize one of the cyclopentadienyl fragments, forming a trisulfanido moiety bound to the metal in an unprecedented η^2 fashion (**47**). Based on the formation of a dithiolene moiety as determined by structural parameters, the mechanism for this transformation is thought to be complex and involves an internal hydrogen migration. The authors make no note of spontaneous desulfurization or decomposition in solution, perhaps due to the chelating nature of the ligand and/or the η^2 interaction of the trisulfane fragment to the metal center. This complex was reported to be obtained in 40% yield among several species, suggesting a complicated mechanism of formation.

While not structurally characterized, **20** was also shown to form trisulfanido complexes by intermolecular nucleophilic attack on carbon electrophiles. Treatment with sulfide (S^{2-}) is proposed to ring-open the pentasulfido chelate and dissociate two sulfur atom equivalents, likely in the form of S_8 (Scheme 19). The resulting metal-bound terminal polysulfido ligands then attack electrophilic substrates such as geminal dihalomethanes or ketones.[139] While the bis(disulfanido) chelate (**48**) was observed to

be the major product upon addition of most electrophiles, the addition of the comparatively unhindered electrophile dibromomethane to this intermediate also yielded the unsymmetric thiolate-trisulfanide chelate (**49**) as a minor product that was isolable by chromatography and was assigned spectroscopically.

In a second example of nucleophilic formation of a trisulfanide moiety, treatment of the hydrosulfido complex $Cp_2Ti(SH)_2$ (**50**) with two equivalents of ArS-imide (Ar = Ph or *p*-tolyl, imide = phthalimide or succinimide) forms a S–S bond between the hydrosulfido moiety and the "ArS^+" moiety to afford the titanium thiolato/trisulfanido complex (**51**, **52**, Scheme 20).[103] The selectivity of this reaction is dependent on the phthalimide substituent; aryl-substituted phthalimides are selective for trisulfanido formation, whereas alkyl analogs yield the bis-disulfanido product (**53**). This selectivity is attributed to the ability of aryl thiolates to act as better leaving groups than alkyl thiolates. In the formation of **51** and **52**, the addition of the first equivalent of ArS-imide forms the mixed disulfanido/hydrosulfido complex $Cp_2Ti(SH)(SSAr)$. This intermediate is proposed to undergo intramolecular nucleophilic attack of the hydrosulfide ligand upon the disulfanide ligand, rearranging to a hydropersulfido intermediate ($Cp_2Ti(SAr)(SSH)$ which proceeds to react with the second equivalent of *N*-(phenyldithio)phthalimide and form the trisulfanido product **51** or **52**. While the trisulfanide moiety was not reported to spontaneously desulfurize in solution to give the disulfanido or thiolate species, the complex was observed to decompose giving mixtures of organopolysulfides, highlighting the general instability of monodentate polysulfanido species.

In a similar reaction, a ruthenium trisulfanido complex (**55**) was generated upon treatment of the hydrosulfido complex **54** with *N*-(propyldithio)phthalimide (Scheme 21).[140] Remarkably, this monodentate trisulfanide ligand is stable in solution and more

resistant to air exposure than its disulfanido analog. This reactivity contrasts to that of the previous titanium trisulfanido examples (**51**, **52**) as well as the similarly synthesized $CpW(CO)_3(S_3R)$ (R = Ch_2Ph or p-$C_6H_4CH_3$),[141] which spontaneously desulfurize in solution. In addition to the structurally characterized 1-propyl-substituted trisulfanido complex, the 2-propyl and 4-methylphenyl analogs were also confirmed spectroscopically and observed to be similarly stable; as such, the factors governing the stability of these linear trisulfanido ligands remain poorly understood.

A zinc tetrasulfanido complex supported by a pentadentate bis(carboxamide)pyridine framework (**57**) was recently shown to form through selective insertion of three atom equivalents of S^0 into one of the Zn−S bonds of a zinc dithiolate complex (**56**) upon treatment with 3/8 equivalents of S_8 (Scheme 22).[142] This complex is currently the only example of a metal tetrasulfanido complex and is also the only metal polysulfanido complex synthesized by S_8 insertion into a metal-organothiolate bond. This complex has been a useful platform for conducting studies on transition metal polysulfanido reactivity and for comparison to the transition metal polysulfido complexes discussed above.

3.3. Stability, Selectivity, and Reactivity of Metal Polysulfanido Complexes

In contrast to metal polysulfido complexes, many of which share well-established synthetic routes, the energetic factors responsible for formation of stable metal polysulfanido complexes is a key unresolved question, as there are fewer examples and fewer general synthetic strategies or precursors. Many reported syntheses are limited in scope to complexes with similar organic substituents terminating the sulfur chain or similar ancillary ligands such as terminal sulfides acting as sulfur donors.

In particular, the factors governing selectivity of polysulfanido ligand speciation (i.e., chain length) are currently unclear. The majority of metal disulfanido and polysulfanido complexes discussed above are chelates; for these examples, ring strain within the metallacycle is likely one energetic factor that dictates selectivity. As a demonstration of selectivity, the abstraction of sulfur from **57** by addition of PPh_3 forms the zinc dithiolate precursor complex **56** even in substoichiometric amounts, with no formation of smaller polysulfanido chelates.[142] Despite this thermodynamic stability, **57** is dynamic in solution; mass spectrometry of an acetonitrile mixture of $^{34}S_8$ and unlabelled **57** shows the expected 1:3:3:1 statistical distribution of masses with 0–3 incorporated ^{34}S atoms within the tetrasulfanido moiety.[143] The 8-membered metallacycle is suggested to play a significant role in the stability of the complex, consistent with the improved stability of chelating di- and trisulfanido ligands compared to the monodentate examples.

The structural data of crystallographically characterized metal disulfanido and polysulfanido complexes (Tables 1 and 2) reveal a range of bond lengths and angles typical of other organic or inorganic sulfur-containing molecules. The lack of exceptional structural parameters from these data suggest other contributors to stability must also be considered.

While a number of other thermodynamic factors have been proposed in discussing syntheses of polysulfanido complexes, particularly stable monodentate species, many of them have proven individually insufficient in predicting general stability. For example, an inverse relationship between the S−S bond dihedral angle and bond length in organic disulfides has been attributed to bond-weakening lone pair-lone pair repulsions that experience a minimum at a dihedral angle of 90°.[144] Some reports have postulatd a similar correlation for metal disulfanido complex stability.[141, 145] In

support of this, crystallographic characterization of the free phenyltetrasulfanide anion shows expected S−S dihedral angles of 88-89°.[116] However, structural data of an air-stable ruthenium disulfanido complex[140] and a copper disulfanido complex[146] with the shortest reported metal polysulfanido S−S bond distance reveal dihedral angles of 78.0° and 98.6°, respectively. Both complexes feature sterically unhindered, monodentate disulfanide ligands, and a survey of metal polysulfanido complexes in the literature also shows no obvious relationship between these parameters, making such generalizations difficult.

Additional factors may further complicate identification of these types of trends, such as the degree of covalency between sulfur and the metal centers. Delocalization of electron density from sulfur onto the metal center or the terminal organic substituent may also impact the overall stability of the ligand. This effect has been demonstrated in computational studies of gas-phase sulfanes[147] and has also been used to explain shortened S−S bond distances of the phenyltetrasulfanide anion in the solid state.[116] The trend of progressively decreasing S−S contact lengths is also evident in the structural data of stable polysulfanido species (Table 2). Electron delocalization may also play an energetic role in the formation of the titanium trisulfanido complexes (**53**, **54**) reported by Shaver and coworkers discussed above, where π-accepting aryl substituents were observed to promote trisulfanide formation vs. the bis(disulfanido) complexes formed with alkyl groups.

Steric protection via the use of bulky organic groups on ancillary ligands to protect reactive functionalities is a common strategy across all fields of coordination chemistry and may be similarly effective in preventing spontaneous desulfurization of polysulfanido ligands. The tris(pyrazolyl)borate zinc disulfanido complexes reported by Artaud and coworkers feature isopropyl (**40**) or phenyl (**41**) groups surrounding the

monodentate disulfanide ligand.[109] However, this hypothesis is complicated by the existence of disulfanido and even trisulfanido complexes with no apparent steric protection, such as the ruthenium propyltrisulfanido complex (**55**) reported by Shaver and coworkers[140] and highlights that such considerations are not a strict requirement for the stability of these compounds. Taken together, there is a clear need for a more complete understanding of the requisite electronic and structural features for stabilizing metal polysulfanido complexes.

Although the reactions of metal polysulfanido complexes have not been extensively studied, certain examples have demonstrated the ability to undergo a variety of sulfur-centered reactions. Oxidation of **57** by one electron results in rearrangement to a bimetallic complex with two ligand equivalents bridged by a diaryl trisulfide moiety—the remaining four sulfur atom equivalents presumably extruded as S_8 (Scheme 23). Reduction of **57** also occurs at sulfur; treatment with cobaltocene regenerates the dithiolate precursor **56**, releasing $S_3^{\cdot -}$.

In contrast to zinc, where redox occurs primarily at the sulfur-containing ligands, the oxidation or reduction of complexes featuring redox-active metals has been shown to affect the S−S bond of a bound disulfanido moiety, as reported in a study of the disulfanide S−S linkage of a Tp-supported Mo^{VI} complex (Scheme 24).[148] Reduction of a Mo^{IV}-oxo-pyridinedisulfanido complex (**58**) breaks the perthiolate S−S bond and forms a reduced terminal sulfide and an overall oxidized Mo^{V} center (**59**). The pyridine-containing ligand also undergoes rearrangement to a monodentate thiolate. Oxidation from the starting disulfanide complex was shown to occur primarily at the metal center (**60**). The tungsten congener (**61**) was later reported with similar transformations (**62**, **63**) and was found to be less reducible than the Mo example.[149] These reports suggest that electron-rich metal centers can better stabilize bound sulfane-

containing species, while more oxidized complexes favor breaking the S—S bond to extrude S^0 or, in the case of the molybdenum or tungsten complexes above, form redox-active terminal sulfide ligands.

In another example of interconversion between sulfido and sulfanido moieties, a disulfido-bridged dirhenium complex (**64**, Scheme 25) reversibly forms a bridged bis-disulfanido species (**65**) in the presence of Lewis acids such as trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) or LiCl.[135] In this reaction, the Re^{IV}-Re^{IV} complex undergoes an induced internal electron transfer in a formal $2e^-$ reduction to form the Re^{III}-Re^{III} trithiocarbamate species. The reverse reaction is possible with reduction of disulfanido back to dithiocarbamate, which oxidizes to the thiuram disulfide during aqueous workup.

Like di/polysulfido ligands, metal polysulfanido moieties are also nucleophilic. Treatment of **57** with iodomethane results in stepwise conversion of the tetrasulfanido and thiolate to the methyl thioethers (Scheme 26). In a more complex reaction, treatment of **57** with dimethylacetylenedicarboxylate (DMAD), known to accept sulfur atoms from metal polysulfides,[93] results in rearrangement to two new zinc complexes (Scheme 26). The first zinc equivalent becomes bound to two ligand equivalents linked by two trisulfide bridges and formally contains two of the three added sulfane atoms of the starting tetrasulfanido complex. The second zinc ion is coordinated by two DMAD-derived dithiolene moieties. Finally, the tetrasulfanido moiety was demonstrated to be a weaker nucleophile compared to the thiolate moieties of both the tetrasulfanido complex (**57**) itself and of the related zinc dithiolate complex (**56**) towards alkyl electrophiles as well as in its ability to catalyze the exchange of alkyl disulfides.[20]

While these reports hint at the broad potential for metal polysulfanido reactivity, the literature still lacks comprehensive study on the mechanism of sulfur insertion,

sulfur abstraction, or nucleophilic reactions of polysulfanide complexes. Important details such as whether sulfur insertion occurs through dissociative or concerted pathways, which sulfur atoms in a polysulfanido chain act as nucleophilic or electrophilic sites, or the effects of metal, ligand, and/or polysulfur chain length on polysulfanido redox potentials may greatly inform future studies on metal polysulfanido complexes.

4. Outlook

4.1. Biologically relevant reactions

Beyond the metal-sulfide, -polysulfide, and -polysulfanide interactions discussed above, there are additional opportunities and open questions in metal-sulfur chemistry that are relevant to biological processes. In particular, the interactions between transition metals and sulfur/NO or sulfur/CO compounds are relevant to biological "crosstalk" between H_2S, CO, and NO, gasotransmitters responsible for biological redox signaling.[150-153] The metal-free interconversions of related compounds and anions have been well studied. For example, S_8 and NO (or NO_2^-) form perthionitrite ($SSNO^-$), polysulfide anions, and other oxidized sulfur and nitrogen products in both aqueous and nonaqueous conditions that have been characterized through a combination of spectroscopic methods.[154-156] Equations 1–3 show selected reactions of these important sulfur-nitrogen species.

$$\tfrac{1}{2}H_2S_2 + NO^{\cdot} \rightleftharpoons HSNO \qquad (1)$$

$$RS_x^{\cdot} + NO^{\cdot} \rightleftharpoons RS_xNO \qquad (2)$$

$$S_8 + NO_2^- \rightleftharpoons S_2NO^- \qquad (3)$$

Transition metal-mediated reactions and interconversions of NO/H_2S cross-talk species have also demonstrated that these cross-talk species are intimately related to the sulfur-

and transition-metal centered redox reactions discussed in previous sections. The existence of relevant, metal-bound intermediates has been inferred from interconversion between S-nitrosothiols and their nitrogen oxide and H_2S or thiol components on dinitrosyl iron complexes (DNICs) or synthetic model complexes.[157-159] Pluth and coworkers have shown that reaction of bioavailable reagents Fe^{2+} and SNO^- or $SSNO^-$ forms mononitrosyl (**66**) or dinitrosyl (**67**) iron complexes, respectively (Scheme 27).[160] Sulfur abstraction from **67** by treatment with PPh_3 afforded a sulfide-bridged diiron complex **68**, implicating these sulfur-containing substrates in the synthesis of biorelevant iron-sulfur clusters. Additionally, nitrosylation of a synthetic $[Fe_4S_4]$ cubane cluster has suggested nitrosyl moieties bound to iron-sulfur clusters are intermediates in biological NO sensing.[161] Nitrosylation has also been implicated in the interconversion between sulfido, thiolato, and disulfanido motifs. Treatment of the dichromium complex **69** featuring bridging sulfido and thiolato ligands with nitric oxide results in transfer of the alkyl thiolate, forming the bridging disulfanido complex **70** (Scheme 28).[162]

S-nitrosothiol compounds are known products of thiolate attack on metal-bound nitrite to release NO and are involved in NO/NO_2^- interconversion. There are a number of structurally characterized synthetic transition metal complexes of such NO/H_2S crosstalk species. For example, metal *S*-nitrosothiol adducts have been isolated and characterized through treatment of iridium nitrosyl with organic thiols[163-164] as well as a tris(pyrazolyl)borate Cu^{II}-bound trityl thiolate that demonstrated reversible NO insertion to form a Cu^{I} *S*-nitrosothiol complex.[158]

Nitrosothiols are known to further react with polysulfides to form perthionitrite, which acts in biology as sulfane, polysulfide, and nitric oxide reserves.[165] However, HSNO, HSSNO, and their respective anions are extremely reactive species that act as nitrosating agents within H_2S/NO crosstalk pathways. Due to their instability, the metal

complexes of these species have been difficult to characterize and study, with the exception of salts with redox-inactive countercations. However, recent studies have demonstrated isolation of transition metal-bound thionitrite and related species. Warren and coworkers reported the synthesis of a tris(pyrazolyl)borate-supported zinc perthionitrite complex via sodium perthionitrite salt (**71**, Scheme 29).[166] Reductive abstraction of one sulfur atom with triphenylphosphine results in both the *anti* and *syn* isomers of the zinc thionitrite complex (**72**). Hayton and coworkers showed that the masked terminal Ni^{2+} and Zn^{2+} sulfido complexes **15** and **16** can capture N_2O to form metal-bound thiohyponitrite moieties (Scheme 30, **73** and **74**). The zinc complex **76** was observed to exhibit longer O−N and shorter N−N distances than the nickel congener, suggesting the contribution of a $[SNN{=}O]^{2-}$ resonance form in addition to $[SN{=}NO]^{2-}$.

The possibility of biorelevant H_2S chemistry with the gasotransmitter CO at metal centers has also been explored. CO dehydrogenase has been proposed to first react by insertion of CO into a Cu–S bond within a [CuSMo(O)OH)] cluster,[167] and sulfide- or thiolate-supported metal carbonyl clusters (e.g. in hydrogenase mimics or CO-terminated iron-sulfur clusters) are well-known, but the conditions that enable CO activation remain unclear. Sita and coworkers have demonstrated that a molybdenum complex supported by Cp* and an amidinate ligand (**75**) can catalytically generate COS from S_8 and CO gas under photoexcitation (Scheme 31).[168] These studies were also extended to isoelectronic isocyanide substrates, which were shown to form isothiocyanates upon reaction with sulfur.[169] Hayton has also studied the reaction of nickel sulfides with CO to yield a coordinated COS ligand.[170]

4.2. Materials and Energy-Related Applications

The advancement of synthetic metal-sulfur complexes and their diverse structural

motifs present new opportunities for materials or colloidal nanomaterials applications. From a synthetic perspective, development of new molecular metal sulfur complexes could be adapted toward more controlled syntheses of metal chalcogenide nanocrystals. Established syntheses of metal sulfide nanocrystals previously relied on the use of reagents like $(Me_3Si)_2S$ and polysulfide solution formed from the reaction between S_8 and amines,[171] while Owen and co-workers demonstrated that the use of different reagents such as thioureas increases synthetic control of product size and dispersity.[172-173] As such, new sulfur transfer reagents may enable the synthesis of next-generation materials including ternary lattices or lead-free chalcogenide perovskites.[174-175] The formation and redox interconversion of metal sulfur species and clusters is also of interest for understanding the monomer species that are involved in colloidal nanomaterials growth. These metal sulfur species are related to nanoparticle nucleation and growth, and as such their speciation and reactivity dynamics are of crucial importance in controlling nanocrystal synthesis.[176] Although metal dithiocarbamates have been used for controlled nanocrystal synthesis, there have been fewer studies for the use of metal polysulfide or polysulfanide species for these syntheses. The use of such compounds as single-source precursors could present an opportunity for controlling the metal:sulfur stoichiometry and redox state that would be of use in controlling the phases of the products.[44]

The sulfur-centered reactions of metal polysulfido and polysulfanido complexes described above may also inform the design of functional motifs for new materials for energy storage applications. For example, sulfur-based electrodes in batteries have been targeted due to their high theoretical energy densities, but commercialization has been challenging due to the solubility and diffusion of polysulfide anions.[177] Many new electrode architectures have been developed as methods for polysulfide and sulfur

sequestrations or capture, with variable success.[178-180] Lessons from transition metal polysulfido and polysulfanido complexes may provide further opportunities in electrode or battery design.

Conclusions

The synthesis of new transition metal-sulfur complexes has advanced over the past several decades, but new coordination motifs and reactions continue to be discovered due to sulfur's versatile bonding and redox reactivity. Understanding the thermodynamic and kinetic factors that govern structural selectivity remains an ongoing challenge that will be important for using these species as relevant models for biological sulfur chemistry or in energy-related applications. In particular, we anticipate that the reactions of polysulfanido complexes can offer opportunities in sulfur transfer catalysis and other sulfur redox transformations, including in cooperative reactions with other small molecules.

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References

[1] Meyer, J. Iron–Sulfur Protein Folds, Iron–Sulfur Chemistry, and Evolution. *J. Biol. Inorg. Chem.* **2008**, *13*, 157-170.

[2] Wächtershäuser, G. From Volcanic Origins of Chemoautotrophic Life to Bacteria, Archaea and Eukarya. *Phil. Trans. R. Soc. B* **2006**, *361*, 1787-1808.

[3] Pietri, R., Román-Morales, E., López-Garriga, J. Hydrogen Sulfide and Hemeproteins: Knowledge and Mysteries. *Antioxid. Redox Signal.* **2010**, *15*, 393-404.

[4] Bostelaar, T., Vitvitsky, V., Kumutima, J., Lewis, B. E., Yadav, P. K., Brunold, T. C., Filipovic, M., Lehnert, N., Stemmler, T. L., Banerjee, R. Hydrogen Sulfide Oxidation by Myoglobin. *J. Am. Chem. Soc.* **2016**, *138*, 8476-8488.

[5] Román-Morales, E., Pietri, R., Ramos-Santana, B., Vinogradov, S. N., Lewis-Ballester, A., López-Garriga, J. Structural Determinants for the Formation of Sulfhemeprotein Complexes. *Biochem. Biophys. Res. Commun.* **2010**, *400*, 489-492.

[6] Zhang, B., Crack, J. C., Subramanian, S., Green, J., Thomson, A. J., Le Brun, N. E., Johnson, M. K. Reversible Cycling between Cysteine Persulfide-Ligated [2Fe-2S] and Cysteine-Ligated [4Fe-4S] Clusters in the FNR Regulatory Protein. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15734-15739.

[7] Lange, M., Ok, K., Shimberg, G. D., Bursac, B., Markó, L., Ivanović-Burmazović, I., Michel, S. L. J., Filipovic, M. R. Direct Zinc Finger Protein Persulfidation by H_2S Is Facilitated by Zn^{2+}. *Angew. Chem. Int. Ed.* **2019**, *58*, 7997-8001.

[8] Stiefel, E. I. Transition Metal Sulfur Chemistry: Biological and Industrial Significance and Key Trends. In *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*, Stiefel, E. I.; Matsumoto, K., Eds. American Chemical Society: Washington, DC, 1996; Vol. 652, pp 2-39.

[9] Parkin, G. Terminal Chalcogenido Complexes of the Transition Metals. In *Progress in Inorganic Chemistry*, 1997; pp 1-165.

[10] Zhadanov, S. I. Sulfur, Selenium, Tellurium, and Polonium. In *Standard Potentials in Aqueous Solution*, Bard, A. J., Ed. Routledge: New York, 1985; pp 93-126.

[11] Solomon, E. I., Hedman, B., Hodgson, K. O., Dey, A., Szilagyi, R. K. Ligand K-Edge X-Ray Absorption Spectroscopy: Covalency of Ligand–Metal Bonds. *Coord. Chem. Rev.* **2005**, *249*, 97-129.

[12] Vineyard, B. D. Mercaptan—Sulfur Reaction. Alkyl Trisulfides. *J. Org. Chem.* **1966**, *31*, 601-602.

[13] Pringle, D. L. The Nature of the Polysulfide Anion. Iowa State University, 1967.

[14] Vineyard, B. D. Versatility and the Mechanism of the n-Butyl-Amine-Catalyzed Reaction of Thiols with Sulfur. *J. Org. Chem.* **1967**, *32*, 3833-3836.

[15] Olsen, F. P., Sasaki, Y. Reactions of Sulfur with Benzylamine. *J. Am. Chem. Soc.* **1970**, *92*, 3812-3813.

[16] Koppenol, W. H., Bounds, P. L. Signaling by Sulfur-Containing Molecules. Quantitative Aspects. *Arch. Biochem. Biophys.* **2017**, *617*, 3-8.

[17] Cuevasanta, E., Lange, M., Bonanata, J., Coitiño, E. L., Ferrer-Sueta, G., Filipovic, M. R., Alvarez, B. Reaction of Hydrogen Sulfide with Disulfide and Sulfenic Acid to Form the Strongly Nucleophilic Persulfide. *J. Biol. Chem.* **2015**, *290*, 26866-26880.

[18] Benchoam, D., Semelak, J. A., Cuevasanta, E., Mastrogiovanni, M., Grassano, J. S., Ferrer-Sueta, G., Zeida, A., Trujillo, M., Möller, M. N., Estrin, D. A., Alvarez, B. Acidity and Nucleophilic Reactivity of Glutathione Persulfide. *J. Biol. Chem.* **2020**, *295*, 15466-15481.

[19] Filipovic, M. R., Zivanovic, J., Alvarez, B., Banerjee, R. Chemical Biology of H_2S Signaling through Persulfidation. *Chem. Rev.* **2018**, *118*, 1253-1337.

[20] Seo, W. T. M., Ballesteros, M., II, Tsui, E. Y. Sulfane Decreases the Nucleophilic Reactivity of Zinc Thiolates: Implications for Biological Reactive Sulfur Species. *J. Am. Chem. Soc.* **2022**, *144*, 20630-20640.

[21] Fehér, F. SECTION 7 - Sulfur, Selenium, Tellurium. In *Handbook of Preparative Inorganic Chemistry (Second Edition)*, Brauer, G., Ed. Academic Press: 1963; pp 341-456.

[22] Hartle, M. D., Pluth, M. D. A Practical Guide to Working with H_2S at the Interface of Chemistry and Biology. *Chem. Soc. Rev.* **2016**, *45*, 6108-6117.

[23] Hartle, M. D., Meininger, D. J., Zakharov, L. N., Tonzetich, Z. J., Pluth, M. D. NBu_4SH Provides a Convenient Source of HS^- Soluble in Organic Solution for H_2S and Anion-Binding Research. *Dalton Trans.* **2015**, *44*, 19782-19785.

[24] Callahan, K. P., Durand, P. J. Reactions of the Vanadyl Group: Synthesis of VS^{2+} and VBr_2^{2+} from VO^{2+} complexes. *Inorg. Chem.* **1980**, *19*, 3211-3217.

[25] Bristow, S., Collison, D., Garner, C. D., Clegg, W. Crystal Structure of the Complex cis-Oxobis[piperidine N-oxido(1–)-NO]thiomolybdenum(VI), Containing a cis-MoOS2+ Group. *J. Chem. Soc., Dalton Trans.* **1983**, 2495-2499.

[26] Young, C. G., Collison, D., Mabbs, F. E., Enemark, J. H. The First Mononuclear Molybdenum(V) Complex with a Terminal Sulfido Ligand: Dichloro[Hydrotris(3,5-Dimethyl-1-Pyrazolyl)Borato]Sulfidomolybdenum. *Inorg. Chem.* **1987**, *26*, 2925-2927.

[27] Donahue, J. P. Thermodynamic Scales for Sulfur Atom Transfer and Oxo-for-Sulfido Exchange Reactions. *Chem. Rev.* **2006**, *106*, 4747-4783.

[28] Matulenko, M. A., Degl'Innocenti, A., Capperucci, A. Bis(trimethylsilyl) Sulfide. In *Encyclopedia of Reagents for Organic Synthesis*.

[29] Liu, H., Liu, Y., Wang, Z., He, P. Facile Synthesis of Monodisperse, Size-Tunable SnS Nanoparticles Potentially for Solar Cell Energy Conversion. *Nanotechnology* **2010**, *21*, 105707.

[30] Smith, D. K., Luther, J. M., Semonin, O. E., Nozik, A. J., Beard, M. C. Tuning the Synthesis of Ternary Lead Chalcogenide Quantum Dots by Balancing Precursor Reactivity. *ACS Nano* **2011**, *5*, 183-190.

[31] Glaser, P., Stewart Jr, O., Atif, R., Asuigui, D. R. C., Swanson, J., Biacchi, A. J., Hight Walker, A. R., Morrison, G., zur Loye, H.-C., Stoll, S. L. Synthesis of Mixed-Valent Lanthanide Sulfide Nanoparticles. *Angew. Chem. Int. Ed.* **2021**, *60*, 23134-23141.

[32] Boulegue, J. Solubility of Elemental Sulfur in Water at 298 K. *Phosphorus Sulfur Relat. Elem.* **1978**, *5*, 127-128.

[33] Wang, R., Shen, B., Sun, H., Zhao, J. Measurement and Correlation of the Solubilities of Sulfur S_8 in 10 Solvents. *J. Chem. Eng. Data* **2018**, *63*, 553-558.

[34] Ren, Y., Shui, H., Peng, C., Liu, H., Hu, Y. Solubility of Elemental Sulfur in Pure Organic Solvents and Organic Solvent–Ionic Liquid Mixtures from 293.15 to 353.15K. *Fluid Ph. Equilibria* **2011**, *312*, 31-36.

[35] Bolton, S. G., Pluth, M. D. Modified Cyclodextrins Solubilize Elemental Sulfur in Water and Enable Biological Sulfane Sulfur Delivery. *Chem. Sci.* **2020**, *11*, 11777-11784.

[36] Garcia, A. C., Zakharov, L. N., Pluth, M. D. Supramolecular Activation of S_8 by Cucurbiturils in Water and Mechanism of Reduction to H_2S by Thiols: Insights into Biological Sulfane Sulfur Trafficking. *J. Am. Chem. Soc.* **2022**, *144*, 15324-15332.

[37] Steudel, R., Holdt, G. Solubilization of Elemental Sulfur in Water by Cationic and Anionic Surfactants. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1358-1359.

[38] Zhang, G., Yi, H., Chen, H., Bian, C., Liu, C., Lei, A. Trisulfur Radical Anion as the Key Intermediate for the Synthesis of Thiophene via the Interaction between Elemental Sulfur and NaOtBu. *Org. Lett.* **2014**, *16*, 6156-6159.

[39] Chivers, T., Elder, P. J. W. Ubiquitous Trisulfur Radical Anion: Fundamentals and Applications in Materials Science, Electrochemistry, Analytical Chemistry and Geochemistry. *Chem. Soc. Rev.* **2013**, *42*, 5996-6005.

[40] Tobishima, S.-I., Yamamoto, H., Matsuda, M. Study on the Reduction Species of Sulfur by Alkali Metals in Nonaqueous Solvents. *Electrochim. Acta* **1997**, *42*, 1019-1029.

[41] Coucouvanis, D., Kanatzidis, M., Simhon, E., Baenziger, N. C. Synthesis, Molecular Structure, and Reactions of Bis(tetraphenylphosphonium) Hexakis(μ-thiophenolato)-tetrachlorotetraferrate(II), $(Ph_4P)_2[Fe_4(SPh)_6Cl_4]$. Its Reactions with Dibenzyl Trisulfide and the Synthesis of the $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_4S_4(Cl)_2(SC_6H_5)_2]^{2-}$ "Cubane"-Type Clusters. *J. Am. Chem. Soc.* **1982**, *104*, 1874-1882.

[42] Hartmann, N. J., Wu, G., Hayton, T. W. Synthesis of a "Masked" Terminal Nickel(II) Sulfide by Reductive Deprotection and its Reaction with Nitrous Oxide. *Angew. Chem. Int. Ed.* **2015**, *54*, 14956-9.

[43] Cha, M., Shoner, S. C., Kovacs, J. A. Nickel-Promoted Reductive Carbon-Sulfur Bond Cleavage: a Model for the First Step in the Reaction Promoted by Methyl Coenzyme M Reductase. *Inorg. Chem.* **1993**, *32*, 1860-1863.

[44] Rhodes, J. M., Jones, C. A., Thal, L. B., Macdonald, J. E. Phase-Controlled Colloidal Syntheses of Iron Sulfide Nanocrystals via Sulfur Precursor Reactivity and Direct Pyrite Precipitation. *Chem. Mater.* **2017**, *29*, 8521-8530.

[45] Brutchey, R. L. Diorganyl Dichalcogenides as Useful Synthons for Colloidal Semiconductor Nanocrystals. *Acc. Chem. Res.* **2015**, *48*, 2918-2926.

[46] Treichel, P. M., Nakagaki, P. C. New Synthetic Strategies for Organometallic Complexes with Thiolate Ligands. *Organometallics* **1986**, *5*, 711-716.
[47] Boustany, K. S., Sullivan, A. B. Chemistry of Sulfur Compounds-VI. A Novel Method for the Preparation of Disulfides. *Tetrahedron Lett.* **1970**, *11*, 3547-3549.
[48] Dirican, D., Pfister, N., Wozniak, M., Braun, T. Reactivity of Binary and Ternary Sulfur Halides towards Transition-Metal Compounds. *Chem. Eur. J.* **2020**, *26*, 6945-6963.
[49] Wagler, T. A., Daunch, W. A., Rinaldi, P. L., Palmer, A. R. Solid State ^{33}S NMR of Inorganic Sulfides. *J. Mag. Res.* **2003**, *161*, 191-197.
[50] Müller, A., Diemann, E., Jostes, R., Bögge, H. Transition Metal Thiometalates: Properties and Significance in Complex and Bioinorganic Chemistry. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 934-955.
[51] Bastian, E. J., Jr., Martin, R. B. Disulfide Vibrational Spectra in the Sulfur-Sulfur and Carbon-Sulfur Stretching Region. *J. Phys. Chem.* **1973**, *77*, 1129-1133.
[52] El Jaroudi, O., Picquenard, E., Demortier, A., Lelieur, J.-P., Corset, J. Polysulfide Anions. I. Structure and Vibrational Spectra of the S_2^{2-} and S_3^{2-} Anions. Influence of the Cations on Bond Length and Angle. *Inorg. Chem.* **1999**, *38*, 2394-2401.
[53] El Jaroudi, O., Picquenard, E., Demortier, A., Lelieur, J.-P., Corset, J. Polysulfide Anions II: Structure and Vibrational Spectra of the S_4^{2-} and S_5^{2-} Anions. Influence of the Cations on Bond Length, Valence, and Torsion Angle. *Inorg. Chem.* **2000**, *39*, 2593-2603.
[54] Steudel, R., Chivers, T. The Role of Polysulfide Dianions and Radical Anions in the Chemical, Physical and Biological Sciences, Including Sulfur-Based Batteries. *Chem. Soc. Rev.* **2019**, *48*, 3279-3319.
[55] Sherbow, T. J., Zakharov, L., Pluth, M. D. Synthesis of Terminal Bis(hydrosulfido) and Disulfido Complexes of Ni(II) from a Geometrically Frustrated Tetrahedral Ni(II) Chloride Complex. *Inorg. Chem.* **2021**, *60*, 8135-8142.
[56] Morton, M. S., Lachicotte, R. J., Vicic, D. A., Jones, W. D. Insertion of Elemental Sulfur and SO2 into the Metal−Hydride and Metal−Carbon Bonds of Platinum Compounds. *Organometallics* **1999**, *18*, 227-234.
[57] Vicic, D. A., Jones, W. D. Modeling the Hydrodesulfurization Reaction at Nickel. Unusual Reactivity of Dibenzothiophenes Relative to Thiophene and Benzothiophene. *J. Am. Chem. Soc.* **1999**, *121*, 7606-7617.
[58] Pluth, M. D., Tonzetich, Z. J. Hydrosulfide Complexes of the Transition Elements: Diverse Roles in Bioinorganic, Cluster, Coordination, and Organometallic Chemistry. *Chem. Soc. Rev.* **2020**, *49*, 4070-4134.
[59] Tonzetich, Z. J. H_2S and Bioinorganic Metal Complexes. In *Hydrogen Sulfide*, 2022; pp 103-141.
[60] Parkin, G. Synthetic Analogues Relevant to the Structure and Function of Zinc Enzymes. *Chem. Rev.* **2004**, *104*, 699-768.
[61] Shaver, A., McCall, J. M. Preparation and variable-temperature NMR studies of the metallocyclosulfanes Cp_2MS_5 and $(Me_5Cp)_2MS_3$, where M = Ti, Zr and Hf. *Organometallics* **1984**, *3*, 1823-1829.
[62] Mukherjee, R. N., Stack, T. D. P., Holm, R. H. Angle Dependence of the Properties of the $[Fe_2X]^{4+}$ Bridge Unit (X = O, S): Structures, Antiferromagnetic Coupling, and Properties in Solution. *J. Am. Chem. Soc.* **1988**, *110*, 1850-1861.
[63] Ott, V. R., Swieter, D. S., Schultz, F. A. Di-μ-oxo, μ-oxo-μ-sulfido, and di-μ-sulfido Complexes of Molybdenum(V) with EDTA, Cysteine, and Cysteine Ester Ligands. Preparation and Electrochemical and Spectral Properties. *Inorg. Chem.* **1977**, *16*, 2538-2545.
[64] Igarashi, R. Y., Laryukhin, M., Dos Santos, P. C., Lee, H.-I., Dean, D. R., Seefeldt, L. C., Hoffman, B. M. Trapping H^- Bound to the Nitrogenase FeMo-Cofactor Active Site during H_2 Evolution: Characterization by ENDOR Spectroscopy. *J. Am. Chem. Soc.* **2005**, *127*, 6231-6241.
[65] Rathnayaka, S. C., Islam, S. M., DiMucci, I. M., MacMillan, S. N., Lancaster, K. M., Mankad, N. P. Probing the Electronic and Mechanistic Roles of the μ^4-Sulfur Atom in a Synthetic CuZ Model System. *Chem. Sci.* **2020**, *11*, 3441-3447.

[66] Benson, M. T., Cundari, T. R., Lim, S. J., Nguyen, H. D., Pierce-Beaver, K. An Effective Core Potential Study of Transition-Metal Chalcogenides. 1. Molecular Structure. *J. Am. Chem. Soc.* **1994**, *116*, 3955-3966.

[67] Howard, W. A., Parkin, G. Terminal oxo, sulfido, selenido, and tellurido complexes of zirconium, (η^5-$C_5Me_4R)_2Zr(E)(NC_5H_5)$: comparison of terminal Zr-E single and Zr:E double-bond lengths. *J. Am. Chem. Soc.* **1994**, *116*, 606-615.

[68] Trnka, T. M., Parkin, G. A Survey of Terminal Chalcogenido Complexes of the Transition Metals: Trends in their Distribution and the Variation of their ME Bond Lengths. *Polyhedron* **1997**, *16*, 1031-1045.

[69] Carney, M. J., Walsh, P. J., Hollander, F. J., Bergman, R. G. Generation of the Highly Reactive Intermediates Cp^*_2Zr:O and Cp^*_2Zr:S: Trapping Reactions with Alkynes, Nitriles, and Dative Ligands. *Organometallics* **1992**, *11*, 761-777.

[70] Sweeney, Z. K., Polse, J. L., Andersen, R. A., Bergman, R. G. Cycloaddition and Nucleophilic Substitution Reactions of the Monomeric Titanocene Sulfido Complex (η^5-$C_5Me_5)_2(C_5H_5N)TiS$. *J. Am. Chem. Soc.* **1998**, *120*, 7825-7834.

[71] Laurie, Stuart H. Thiomolybdates — Simple but Very Versatile Reagents. *Eur. J. Inorg. Chem.* **2000**, *2000*, 2443-2450.

[72] Diemann, E., Müller, A. Thio and Seleno Compounds of the Transition Metals with the d^0 Configuration. *Coord. Chem. Rev.* **1973**, *10*, 79-122.

[73] Young, C. G., Roberts, S. A., Ortega, R. B., Enemark, J. H. Mononuclear Oxo- and Sulfidomolybdenum(IV) Complexes: Syntheses and Crystal Structures of $[HB(Me_2C_3N_2H)_3]MoE(S_2CNEt_2)$ (E = O, S) and Related Complexes. *J. Am. Chem. Soc.* **1987**, *109*, 2938-2946.

[74] Rabinovich, D., Parkin, G. The Syntheses, Structures, and Reactivity of Monomeric Tungsten(IV) and Tungsten(VI) Bis(sulfido) Complexes: Facile Elimination of Hydrogen from Hydrogen Sulfide. *J. Am. Chem. Soc.* **1991**, *113*, 5904-5905.

[75] Goodman, J. T., Rauchfuss, T. B. Binding of Alkenes to ReS_4. *J. Am. Chem. Soc.* **1999**, *121*, 5017-5022.

[76] Dopke, J. A., Wilson, S. R., Rauchfuss, T. B. Influence of H_2S and Thiols on the Binding of Alkenes and Alkynes to ReS^{4-}: The Spectator Sulfide Effect. *Inorg. Chem.* **2000**, *39*, 5014-5021.

[77] Schwarz, D. E., Rauchfuss, T. B. The Addition of Isocyanides to ReS^{4-}: 3+1 Cycloaddition to S=M=S. *Chem. Commun.* **2000**, 1123-1124.

[78] Goodman, J. T., Inomata, S., Rauchfuss, T. B. Addition of Alkynes and Alkenes to ReS^{4-}: Reactivity Akin to OsO_4. *J. Am. Chem. Soc.* **1996**, *118*, 11674-11675.

[79] Chiu, W. H., Zhang, Q. F., Williams, I. D., Leung, W. H. Addition of Dimethyl Acetylenedicarboxylate to the WSe_4(2-) Anion. *Organometallics* **2010**, *29*, 2631-2633.

[80] Drew, M. G. B., Mitchell, P. C. H., Pygall, C. F. Reaction between Molybdate(VI), Cyanide, and Hydrogen Sulfide. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 784-785.

[81] Baeza Cinco, M. Á., Hayton, T. W. Progress toward the Isolation of Late Metal Terminal Sulfides. *Eur. J. Inorg. Chem.* **2020**, *2020*, 3613-3626.

[82] Vicic, D. A., Jones, W. D. Evidence for the Existence of a Late-Metal Terminal Sulfido Complex. *J. Am. Chem. Soc.* **1999**, *121*, 4070-4071.

[83] Shanahan, J. P., Vicic, D. A., Brennessel, W. W., Jones, W. D. Trapping of a Late-Metal Terminal Sulfido Intermediate with Phenyl Isothiocyanate. *Organometallics* **2022**.

[84] Larsen, P. L., Gupta, R., Powell, D. R., Borovik, A. S. Chalcogens as Terminal Ligands to Iron: Synthesis and Structure of Complexes with Fe^{III}–S and Fe^{III}–Se Motifs. *J. Am. Chem. Soc.* **2004**, *126*, 6522-6523.

[85] Baeza Cinco, M. Á., Wu, G., Kaltsoyannis, N., Hayton, T. W. Synthesis of a "Masked" Terminal Zinc Sulfide and Its Reactivity with Brønsted and Lewis Acids. *Angew. Chem. Int. Ed.* **2020**, *59*, 8947-8951.

[86] Hossain, K., Majumdar, A. Polysulfido Chain in Binuclear Zinc(II) Complexes. *Inorg. Chem.* **2022**, *61*, 6295-6310.

[87] Draganjac, M., Rauchfuss, T. B. Transition Metal Polysulfides: Coordination Compounds with Purely Inorganic Chelate Ligands. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 742-757.

[88] Rauchfuss, T. B. Research on Soluble Metal Sulfides: From Polysulfido Complexes to Functional Models for the Hydrogenases. *Inorg. Chem.* **2004**, *43*, 14-26.

[89] Hofmann, K. A., Höchtlen, F. Krystallisirte Polysulflde von Schwermetallen. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3090-3092.

[90] Wickenden, A. E., Krause, R. A. Polysulfide Chelates. II. Desulfuration of PtS_{15}^{2-} and the synthesis of PtS_{10}^{2-}. *Inorg. Chem.* **1969**, *8*, 779-783.

[91] Coucouvanis, D., Patil, P. R., Kanatzidis, M. G., Detering, B., Baenziger, N. C. Synthesis and Reactions of Binary Metal Sulfides. Structural Characterization of the $[(S_4)_2Zn]^{2-}$, $[(S_4)_2Ni]^{2-}$, $[(S_5)Mn(S_6)]^{2-}$, and $[(CS_4)_2Ni]^{2-}$ Anions. *Inorg. Chem.* **1985**, *24*, 24-31.

[92] Verma, A. K., Rauchfuss, T. B., Wilson, S. R. Donor Solvent Mediated Reactions of Elemental Zinc and Sulfur, sans Explosion. *Inorg. Chem.* **1995**, *34*, 3072-3078.

[93] Pafford, R. J., Rauchfuss, T. B. Effect of Ancillary Ligands on the Reactivity and Structure of Zinc Polysulfido Complexes. *Inorg. Chem.* **1998**, *37*, 1974-1980.

[94] Verma, A. K., Rauchfuss, T. B. Chalcogenospecific Synthesis of 1,2-Se_2S_6 Using ZnS_6(TMEDA). *Inorg. Chem.* **1995**, *34*, 6199-6201.

[95] Zhang, F. J., Zhang, J., Zhou, X. G. Facile Construction of Yttrium Pentasulfides from Yttrium Alkyl Precursors: Synthesis, Mechanism, and Reactivity. *Inorg. Chem.* **2017**, *56*, 2070-2077.

[96] Sherbow, T. J., Zakharov, L. N., Johnson, D. W., Pluth, M. D. Hydrosulfide Oxidation at a Molybdenum Tetrasulfido Complex. *Inorg. Chem.* **2020**, *59*, 15574-15578.

[97] Sweeney, Z. K., Polse, J. L., Bergman, R. G., Andersen, R. A. Dihydrogen Activation by Titanium Sulfide Complexes. *Organometallics* **1999**, *18*, 5502-5510.

[98] Iluc, V. M., Laskowski, C. A., Brozek, C. K., Harrold, N. D., Hillhouse, G. L. Monomeric and Dimeric Disulfide Complexes of Nickel(II). *Inorg. Chem.* **2010**, *49*, 6817-6819.

[99] Yao, S. A., Martin-Diaconescu, V., Infante, I., Lancaster, K. M., Götz, A. W., DeBeer, S., Berry, J. F. Electronic Structure of Ni_2E_2 Complexes (E = S, Se, Te) and a Global Analysis of M_2E_2 Compounds: A Case for Quantized E_2^{n-} Oxidation Levels with n = 2, 3, or 4. *J. Am. Chem. Soc.* **2015**, *137*, 4993-5011.

[100] Coucouvanis, D., Draganjac, M. E., Koo, S. M., Toupadakis, A., Hadjikyriacou, A. I. Reactivity of the molybdenum-polysulfide functional groups in thio- and oxothiomolybdate complexes toward carbon disulfide. Synthesis and reactivity of trithio- and perthiocarbonate complexes of Mo(IV) and Mo(V) and structural characterization of trans-[Ph4P]2[Mo(S)(CS4)2].cntdot.DMF (I), cis-[Ph4P][Et4N][Mo(S)(CS4)2] (II), cis-syn-[Ph4P]2[Mo2(S)2(.mu.-S)2(CS4)2].cntdot.1/2DMF (III), syn-[Ph4P]2[Mo2(S)2(.mu.-S)2(CS3)2] (IV), and syn-[Et4N]2(Mo2(O)2(.mu.-S)2(CS4)(CS3)] (V). *Inorg. Chem.* **1992**, *31*, 1186-1196.

[101] Coucouvanis, D., Draganjac, M. The Formation of Perthiocarbonate Ligands following the Addition of CS_2 to Binary Molybdenum-Sulfur Complexes. The Crystal and Molecular Structures of the $(Ph_4P)_2[(CS_4)_2MoS]$.DMF and $(Ph_4P)_2[(CS_4)Mo_2S_4(CS_4)]$.1/2DMF Complexes. *J. Am. Chem. Soc.* **1982**, *104*, 6820-6822.

[102] Shaver, A., Lai, R. D. Synthesis and Characterization of the Disulfanoplatinum Complexes cis-$(PPh_3)_2$Pt(phth)SSR, where phth = Phthalimido and R = CH_2Ph, $CH_2CH_2CH_3$, $CHMe_2$, *p*-C_6H_4Me, phth. *Inorg. Chem.* **1988**, *27*, 4664-4668.

[103] Shaver, A., McCall, J. M., Bird, P. H., Ansari, N. Preparation and Structure of (η-$C_5H_5)_2$Ti(SPh)(SSSPh): the Product of a Sulfur Catenation Reaction. *Organometallics* **1983**, *2*, 1894-1896.

[104] Shaver, A., Morris, S. Disulfanido Ligands: Preparation and Reactions of Cp_2Ti(SSR)X, where X = SR, Phthalimido, and Cl and R = Alkyl and Aryl Groups. *Inorg. Chem.* **1991**, *30*, 1926-1930.

[105] Galardon, E., Deschamps, P., Tomas, A., Roussel, P., Artaud, I. An Alternate Route to Disulfanido Complexes by Nucleophilic Attack of Thiolates on Ruthenium-bound Thiosulfonato Ligands. *Inorg. Chem.* **2010**, *49*, 9119-21.

[106] Haines, R. J., De Beer, J. A., Greatrex, R. Reactions of Metal Carbonyl Derivatives: XVII. Tri- as well as Di-nuclear Products from the Reactions of Bis(dicarbonyl-η-cyclopentadienyliron) with Various Dialkyl Disulphides. *J. Organomet. Chem.* **1975**, *85*, 89-99.

[107] Aubart, M. A., Bergman, R. G. Reaction of Organic Disulfides with Cobalt-Centered Metal Radicals. Use of the E- and C-Based Dual-Parameter Substituent Model and Quantitative Solvent Effect Analyses To Compare Outer-Sphere and Inner-Sphere Electron-Transfer Processes. *J. Am. Chem. Soc.* **1998**, *120*, 8755-8766.

[108] Liaw, W.-F., Chen, C.-H., Lee, G.-H., Peng, S.-M. Iron Pyridine-2-thiolate Complexes: Interconversion of $[Fe^{0}(CO)_4(SC_5H_4N)]^-$, *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$, and $[Fe^{II}(SC_5H_4N)_3]$. *Organometallics* **1998**, *17*, 2370-2372.

[109] Galardon, E., Tomas, A., Selkti, M., Roussel, P., Artaud, I. Synthesis, Characterization, and Reactivity of Alkyldisulfanido Zinc Complexes. *Inorg. Chem.* **2009**, *48*, 5921-7.

[110] Benaïchouche, M., Bosser, G., Paris, J., Auger, J., Plichon, V. Formation of Stable Aryldisulphide Ions in Dimethylacetamide from the Reaction of Sulphur with Thiolate Ions. *J. Chem. Soc., Perkin Trans. 2* **1990**, 31-36.

[111] Benaïchouche, M., Bosser, G., Paris, J., Plichon, V. Relative Nucleophilicities of Aryldisulphide and Thiolate Ions in Dimethylacetamide Estimated from their Reaction Rates with Alkyl Halides. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1421-1424.

[112] Bosser, G., Benaichouche, M., Coudert, R., Paris, J. Nucleophilic Displacement of the Nitro-Group of Dinitrobenzenes by Electrogenerated Polysulfide Ions in Dimethylacetamide. *New. J. Chem.* **1994**, *18*, 511-517.

[113] Robert, J., Anouti, M., Bosser, G., Parrain, J. L., Paris, J. Displacement of Aromatic Nitro-Groups by Anionic Sulfur Nucleophiles - Reactivity of Aryl Disulfide and Thiolate Ions Towards Dinitrobenzenes in N,N-Dimethylacetamide. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1639-1644.

[114] Bosser, G., Anouti, M., Paris, J. Formation and Scission of the Sulfur-Sulfur Bond: A New Approach to Reactions Between Sulfur/Polysulfide Ions and Thiolate Ions/Disulfides in N,N-Dimethylacetamide. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1993-1999.

[115] Krautscheid, U., Dev, S., Krautscheid, H., Paul, P. P., Wilson, S. R., Rauchfuss, T. B. N-Methylimidazole Mediated Chemistry of Transition Metal Phenylthiolates. The Isolation of the Perthiolate Salts $[M(N\text{-}MeIm)_6](S_2Ph)_2$. *Z. Naturforsch. B* **1993**, *48*, 653-658.

[116] Jungen, S., Paenurk, E., Chen, P. Synthesis, Spectroscopic, and Structural Characterization of Organyl Disulfanides and a Tetrasulfanide. *Inorg. Chem.* **2020**, *59*, 12322-12336.

[117] Bauer, A., Capps, K. B., Wixmerten, B., Abboud, K. A., Hoff, C. D. The Enthalpy of Insertion of Sulfur into the Metal−Hydrogen Bond. Synthetic, Structural, and Calorimetric Study of the Complexes $HS{-}M(CO)_3C_5R_5$ [M = Cr, Mo, W; R = H, Me]. *Inorg. Chem.* **1999**, *38*, 2136-2142.

[118] Fackler, J. P., Jr., Coucouvanis, D., Fetchin, J. A., Seidel, W. C. Sulfur Chelates. VIII. Oxidative Addition of Sulfur to Dithioaryl Acid Complexes of Nickel(II) and Zinc(II). *J. Am. Chem. Soc.* **1968**, *90*, 2784-2788.

[119] Fackler, J. P., Jr., Fetchin, J. A., Fries, D. C. Sulfur Chelates. XV. Sulfur Addition and Abstraction Reactions of Dithioaryl Acid Complexes of Zinc(II), Nickel(II), Palladium(II), and Platinum(II) and the X-ray Crystal Structures of Bis(trithioperoxycumato)zinc(II) and Dithiocumato(trithioperoxycumato)nickel(II). *J. Am. Chem. Soc.* **1972**, *94*, 7323-7333.

[120] Legzdins, P., Sanchez, L. Insertion of Elemental Sulfur into Tungsten-Carbon Bonds. *J. Am. Chem. Soc.* **1985**, *107*, 5525-5526.

[121] Ji, X., Yang, D., Tong, P., Li, J., Wang, B., Qu, J. C–H Activation of Cp* Ligand Coordinated to Ruthenium Center: Synthesis and Reactivity of a Thiolate-Bridged

Diruthenium Complex Featuring Fulvene-like Cp* Ligand. *Organometallics* **2017**, *36*, 1515-1521.

[122] Wu, X., Bose, K. S., Sinn, E., Averill, B. A. Isolation and X-ray Structure of an Intermediate in the Reaction of $(\mu\text{-S})_2Fe_2(CO)_6$ with thiolates: the $[(\mu\text{-S})(\mu\text{-S}_2\text{-tert-Bu})Fe_2(CO)_6]^-$ Ion. *Organometallics* **1989**, *8*, 251-253.

[123] Brunner, H., Graßl, R., Wachter, J., Nuber, B., Ziegler, M. L. Synthese und strukturelle charakterisierung von bis(pentamethylcyclopentadienylmolybdän-μ-sulfido)-komplexen mit μ,η^1-SSR-liganden. *J. Organomet. Chem.* **1992**, *427*, 57-62.

[124] Song, L.-C., Lu, G.-L., Hu, Q.-M., Sun, J. Synthesis of Double and Quadruple Butterfly Fe/S Cluster Complexes via a Novel Type of Reaction of Anions (μ-RS)(μ-S-)$[Fe_2(CO)_6]_2(\mu_4\text{-S})$ with Succinyl Chloride. *Organometallics* **1999**, *18*, 5429-5431.

[125] Alper, H., Sibtain, F., Einstein, F. W. B., Willis, A. C. Remarkable Phase-Transfer-Catalyzed Reactions Involving Sulfur. *Organometallics* **1985**, *4*, 604-606.

[126] Manotti Lanfredi, A. M., Tiripicchio, A., Marsich, N., Camus, A. Perthiocarboxylate Complex. Synthesis, Structure and Spectroscopic Characterization of the Tetrameric Copper(I) *o*-Tolylperthiocarboxylate, $[Cu(S)SSCC_7H_7]_4$. *Inorg. Chim. Acta* **1988**, *142*, 269-275.

[127] Coucouvanis, D., Kanodia, S., Swenson, D., Chen, S. J., Stuedemann, T., Baenziger, N. C., Pedelty, R., Chu, M. Mixed-Valence Coinage Metal Clusters with 1,1-Thioperthio Ligands. Syntheses and Molecular Structures of the Copper and Gold $[Cu_4L_3]^{2-}$, $[Cu_5L_4]^-$, and $[AuCu_4L_4]^-$ Anions (L = 1,1-dicarbo-tert-butoxyethylene-2,2-thioperthiolate). A Geometrically-Locked, Charge-Separated Valence State in the $[Cu_5L_4]^-$ Anion. *J. Am. Chem. Soc.* **1993**, *115*, 11271-11278.

[128] Huang, K.-C., Tsai, Y.-C., Lee, G.-H., Peng, S.-M., Shieh, M. Syntheses and X-ray Structures of a Series of Chalcogen-Containing Manganese Carbonylates $[E_2Mn_3(CO)_9]^-$, $[E_8C_2Mn_2(CO)_6]^{2-}$, and $[E_2Mn_4(CO)_{12}]^{2-}$ (E = Se, S). *Inorg. Chem.* **1997**, *36*, 4421-4425.

[129] Zhao, P., Gray, D. L., Rauchfuss, T. B. Rational Synthesis of the Carbonyl(perthiolato)diiron $[Fe_2(S_3CPh_2)(CO)_6]$ and Related Complexes. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2681-2683.

[130] Rao, C. E., Barik, S. K., Yuvaraj, K., Bakthavachalam, K., Roisnel, T., Dorcet, V., Halet, J.-F., Ghosh, S. Reactivity of CS2 – Syntheses and Structures of Transition-Metal Species with Dithioformate and Methanedithiolate Ligands. *Eur. J. Inorg. Chem.* **2016**, *2016*, 4913-4920.

[131] Beltrán, T. F., Zaragoza, G., Delaude, L. Small Iron-Carbonyl Clusters Bearing Imidazolium-2-trithioperoxycarboxylate Ligands. *Dalton Trans.* **2017**, *46*, 13002-13009.

[132] Maheu, L. J., Pignolet, L. H. X-ray Crystal and Molecular Structure of Tris(*N,*N-diethyldithiocarbamato)-bis[μ-(*N*,*N*-diethyltrithiocarbamato)]-diosmium(III) Tetraphenylborate. The First Example of a Sulfur-Rich Dithiocarbamate. *Inorg. Chem.* **1979**, *18*, 3626-3629.

[133] Troyano, J., Corral, I., Castillo, O., Zamora, F., Mas-Ballesté, R., Delgado, S. S–S Bond Activation in Multi-Copper -Aggregates Containing Perthiocarboxylato Ligands. *Eur. J. Inorg. Chem.* **2015**, *2015*, 4044-4054.

[134] Mallick, S., Garu, P., Chowdhury, J., Saha, R., Chattopadhyay, S. Dirhenium(III,III) Trithiocarbamato Complexes: Experimental and Theoretical Investigation. *Transition Met. Chem.* **2021**, *46*, 583-591.

[135] Wei, L., Halbert, T. R., Murray, H. H., III, Stiefel, E. I. Induced Internal Electron Transfer Reactiviy of Tetrathioperrhenate(VII): Synthesis of the Interconvertible Dimers $Re_2(\mu\text{-S})_2(S_2CNR_2)_4$ and $[Re_2(\mu\text{-SS}_2CNR_2)_2(S_2CNR_2)_3][O_3SCF_3]$ (R = Me, iso-Bu). *J. Am. Chem. Soc.* **1990**, *112*, 6431-6433.

[136] Tzeng, B.-C., Chao, A., Banik, M. Ligand-Coupling Assembly of Re(I)-thiolate Complexes. *Dalton Trans.* **2014**, *43*, 11510-11515.

[137] Hossain, M. I., Ghosh, S., Hogarth, G., Kabir, S. E. Reactions of $M_2(CO)_9L$ (M = Re, Mn; L = CO, MeCN) with Thioacetamide and Thiobenzamide: Facile Metal-Mediated Nitrogen-Hydrogen Bond Activation and Subsequent Carbon-Nitrogen or Sulfur-Sulfur Bond Formation. *J. Organomet. Chem.* **2013**, *737*, 53-58.

[138] Giolando, D. M., Rauchfuss, T. B., Wilson, S. R. Rearrangement of the Titanocene Derivative $(C_5H_5)_2TiS_5$ Involving Migration of the Organic Fragment from Metal to Sulfur. *J. Am. Chem. Soc.* **1984**, *106*, 6455-6456.

[139] Giolando, D. M., Rauchfuss, T. B. Alkylidenebis(perthiolates): a New Class of Organosulfur Ligands Prepared from $(RC_5H_4)_2TiS_5$. *Organometallics* **1984**, *3*, 487-489.

[140] Shaver, A., Plouffe, P.-Y. Polysulfanido Ligands: The Preparation and Structures of Complexes of the Type $CpRu(PPh_3)(CO)S_xR$, Possessing Disulfanido (x = 2) and Trisulfanido (x = 3) Ligands. *Inorg. Chem.* **1994**, *33*, 4327-4333.

[141] Shaver, A., Hartgerink, J. The Preparation and Characterization of Polysulfanotungsten Complexes of the Type $(\eta^5\text{-}C_5H_5)W(CO)_3S_xR$, where x = 2, 3 and $(\eta^5\text{-}C_5H_5)W(CO)_3SS(O)R$, where R = $CH_2C_6H_5$, *p*-$C_6H_4CH_3$. *Can. J. Chem.* **1987**, *65*, 1190-1194.

[142] Ballesteros, M., Tsui, E. Y. Reactivity of Zinc Thiolate Bonds: Oxidative Organopolysulfide Formation and S_3 Insertion. *Inorg. Chem.* **2019**, *58*, 10501-10507.

[143] Ballesteros, M. T., E. Y. Sulfur Transfer Reactions of a Zinc Tetrasulfanido Complex. *Dalton Trans.* **2020**, *49*, 16305-16311.

[144] Hordvik, A., Grjotheim, K., Krohn, C., Motzfeldt, K., Williams, D. H., Bunnenberg, E., Djerassi, C., Records, R. Bond-length/Dihedral-angle and Bond-length/Bond-order Relationships for Sulphur(II)-Sulphur(II) Bonds. *Acta Chem. Scand.* **1966**, *20*, 1885-1891.

[145] Shaver, A., Hartgerink, J., Lai, R. D., Bird, P., Ansari, N. Catenated Sulfur Ligands: the Synthesis of Metal Disulfanes and the Structures of *cis*-$(PPh_3)_2Pt(C_8H_4NO_2)SSCH(CH_3)_2$ and $(\eta^5\text{-}C_5H_5)W(CO)_3SS\text{-}p\text{-}C_6H_4CH_3$. *Organometallics* **1983**, *2*, 938-940.

[146] John, E., Bharadwaj, P. K., Krogh-Jespersen, K., Potenza, J. A., Schugar, H. J. Molecular and Electronic Structure of $Cu(tet\text{-}b)SSCH_2CO_2\cdot 3CH_3OH$, a Novel Copper(II) Alkyl Persulfide Complex. *J. Am. Chem. Soc.* **1986**, *108*, 5015-5017.

[147] Otto, A. H., Steudel, R. The Gas Phase Acidities of the Sulfanes H_2S_n (n = 1–4). *Eur. J. Inorg. Chem.* **1999**, *1999*, 2057-2061.

[148] Hill, J. P., Laughlin, L. J., Gable, R. W., Young, C. G. Degree and Influence of MoS··S Interactions in Oxo−Molybdenum(VI,V,IV) Complexes. *Inorg. Chem.* **1996**, *35*, 3447-3448.

[149] Thomas, S., Eagle, A. A., Sproules, S. A., Hill, J. P., White, J. M., Tiekink, E. R. T., George, G. N., Young, C. G. Redox Interplay of Oxo−Thio−Tungsten Centers with Sulfur-Donor Co-Ligands. *Inorganic Chemistry* **2003**, *42*, 5909-5916.

[150] Abe, K., Kimura, H. The Possible Role of Hydrogen Sulfide as an Endogenous Neuromodulator. *J. Neurosci.* **1996**, *16*, 1066.

[151] Wang, R. Gasotransmitters: Growing Pains and Joys. *Trends Biochem. Sci.* **2014**, *39*, 227-232.

[152] Coletta, C., Papapetropoulos, A., Erdelyi, K., Olah, G., Módis, K., Panopoulos, P., Asimakopoulou, A., Gerö, D., Sharina, I., Martin, E., Szabo, C. Hydrogen Sulfide and Nitric Oxide are Mutually Dependent in the Regulation of Angiogenesis and Endothelium-dependent Vasorelaxation. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 9161-6.

[153] Filipovic, M. R., Miljkovic, J. L., Nauser, T., Royzen, M., Klos, K., Shubina, T., Koppenol, W. H., Lippard, S. J., Ivanović-Burmazović, I. Chemical Characterization of the Smallest S-Nitrosothiol, HSNO; Cellular Cross-talk of H_2S and S-Nitrosothiols. *J. Am. Chem. Soc.* **2012**, *134*, 12016-12027.

[154] Marcolongo, J. P., Venâncio, M. F., Rocha, W. R., Doctorovich, F., Olabe, J. A. NO/H_2S "Crosstalk" Reactions. The Role of Thionitrites (SNO^-) and Perthionitrites ($SSNO^-$). *Inorg. Chem.* **2019**, *58*, 14981-14997.

[155] Cortese-Krott, M. M., Butler, A. R., Woollins, J. D., Feelisch, M. Inorganic Sulfur-Nitrogen Compounds: from Gunpowder Chemistry to the Forefront of Biological Signaling. *Dalton Trans.* **2016**, *45*, 5908-5919.

[156] Seel, F., Wagner, M. Über die Umsetzung von Polysulfiden mit Stickstoffmonoxid in nichtwäßrigen Lösungsmitteln — Nitrosodisulfide *Z. Naturforsch. B* **1985**, *40b*, 762-764.

[157] Jordan, A. J., Walde, R. K., Schultz, K. M., Bacsa, J., Sadighi, J. P. Nitrosonium Reactivity of (NHC)Copper(I) Sulfide Complexes. *Inorg. Chem.* **2019**, *58*, 9592-9596.
[158] Zhang, S., Melzer, M. M., Sen, S. N., Çelebi-Ölçüm, N., Warren, T. H. A Motif for Reversible Nitric Oxide Interactions in Metalloenzymes. *Nat. Chem.* **2016**, *8*, 663-669.
[159] Tian, S., Liu, J., Cowley, R. E., Hosseinzadeh, P., Marshall, N. M., Yu, Y., Robinson, H., Nilges, M. J., Blackburn, N. J., Solomon, E. I., Lu, Y. Revesible S-nitrosylation in an Engineered Azurin. *Nat. Chem.* **2016**, *8*, 670-677.
[160] Sherbow, T. J., Fu, W., Tao, L., Zakharov, L. N., Britt, R. D., Pluth, M. D. Thionitrite (SNO^-) and Perthionitrite ($SSNO^-$) are Simple Synthons for Nitrosylated Iron Sulfur Clusters. *Angew. Chem. Int. Ed.* **2022**, *61*, e202204570.
[161] Kim, Y., Sridharan, A., Suess, D. L. M. The Elusive Mononitrosylated $[Fe_4S_4]$ Cluster in Three Redox States. *Angew. Chem. Int. Ed.* **2022**, *61*, e202213032.
[162] Eremenko, I. L., Pasynskii, A. A., Kalinnikov, V. T., Struchkov, Y. T., Aleksandrov, G. G. Nitrosylation of Dicyclopentadienyldi(μ-tert-butylthiolato)(μ-sulfido)dichromium Giving Tert-butylsulfanic Group. Molecular Structures of the Binuclear Complex $Cp(NO)Cr(\mu\text{-}SCMe_3)(\mu\text{-}S\text{-}SCMe_3)Cr(NO)Cp$ and Monomer $CpCr(NO)_2(ONO)$. *Inorg. Chim. Acta* **1981**, *52*, 107-111.
[163] Perissinotti, L. L., Estrin, D. A., Leitus, G., Doctorovich, F. A Surprisingly Stable S-Nitrosothiol Complex. *J. Am. Chem. Soc.* **2006**, *128*, 2512-2513.
[164] Perissinotti, L. L., Leitus, G., Shimon, L., Estrin, D., Doctorovich, F. A Unique Family of Stable and Water-Soluble S-Nitrosothiol Complexes. *Inorg. Chem.* **2008**, *47*, 4723-4733.
[165] Cortese-Krott, M. M., Kuhnle, G. G. C., Dyson, A., Fernandez, B. O., Grman, M., DuMond, J. F., Barrow, M. P., McLeod, G., Nakagawa, H., Ondrias, K., Nagy, P., King, S. B., Saavedra, J. E., Keefer, L. K., Singer, M., Kelm, M., Butler, A. R., Feelisch, M. Key Bioactive Reaction Products of the NO/H_2S Interaction are S/N-hybrid Species, Polysulfides, and Nitroxyl. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, E4651-E4660.
[166] Hosseininasab, V., Bertke, J. A., Warren, T. H. Thionitrite and Perthionitrite in NO Signaling at Zinc. *Angew. Chem. Int. Ed.* **2021**, *60*, 21184-21188.
[167] Dobbek, H., Gremer, L., Kiefersauer, R., Huber, R., Meyer, O. Catalysis at a Dinuclear [CuSMo(O)OH] Cluster in a CO Dehydrogenase Resolved at 1.1-Å Resolution. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 15971-15976.
[168] Farrell, W. S., Zavalij, P. Y., Sita, L. R. Metal-Catalyzed "On-Demand" Production of Carbonyl Sulfide from Carbon Monoxide and Elemental Sulfur. *Angew. Chem. Int. Ed.* **2015**, *54*, 4269-4273.
[169] Farrell, W. S., Zavalij, P. Y., Sita, L. R. Catalytic Production of Isothiocyanates via a Mo(II)/Mo(IV) Cycle for the "Soft" Sulfur Oxidation of Isonitriles. *Organometallics* **2016**, *35*, 2361-2366.
[170] Hartmann, N. J., Wu, G., Hayton, T. W. Reactivity of a Nickel Sulfide with Carbon Monoxide and Nitric Oxide. *J. Am. Chem. Soc.* **2016**, *138*, 12352-12355.
[171] Thomson, J. W., Nagashima, K., Macdonald, P. M., Ozin, G. A. From Sulfur−Amine Solutions to Metal Sulfide Nanocrystals: Peering into the Oleylamine−Sulfur Black Box. *J. Am. Chem. Soc.* **2011**, *133*, 5036-5041.
[172] Hendricks, M. P., Campos, M. P., Cleveland, G. T., Jen-La Plante, I., Owen, J. S. A Tunable Library of Substituted Thiourea Precursors to Metal Sulfide Nanocrystals. *Science* **2015**, *348*, 1226-1230.
[173] Hamachi, L. S., Jen-La Plante, I., Coryell, A. C., De Roo, J., Owen, J. S. Kinetic Control over CdS Nanocrystal Nucleation Using a Library of Thiocarbonates, Thiocarbamates, and Thioureas. *Chem. Mater.* **2017**, *29*, 8711-8719.
[174] Rosales, B. A., White, M. A., Vela, J. Solution-Grown Sodium Bismuth Dichalcogenides: Toward Earth-Abundant, Biocompatible Semiconductors. *J. Am. Chem. Soc.* **2018**, *140*, 3736-3742.
[175] Zilevu, D., Creutz, S. E. Shape-Controlled Synthesis of Colloidal Nanorods and Nanoparticles of Barium Titanium Sulfide. *Chem. Mater.* **2021**, *33*, 5137-5146.

[176] Campos, M. P., De Roo, J., Greenberg, M. W., McMurtry, B. M., Hendricks, M. P., Bennett, E., Saenz, N., Sfeir, M. Y., Abécassis, B., Ghose, S. K., Owen, J. S. Growth Kinetics Determine the Polydispersity and Size of PbS and PbSe Nanocrystals. *Chem. Sci.* **2022**, *13*, 4555-4565.
[177] Manthiram, A., Fu, Y., Chung, S.-H., Zu, C., Su, Y.-S. Rechargeable Lithium–Sulfur Batteries. *Chem. Rev.* **2014**, *114*, 11751-11787.
[178] Banerjee, S., Han, X., Siegler, M. A., Miller, E. M., Bedford, N. M., Bukowski, B. C., Thoi, V. S. Flexible 2D Boron Imidazolate Framework for Polysulfide Adsorption in Lithium–Sulfur Batteries. *Chem. Mater.* **2022**, *34*, 10451-10458.
[179] Jayaprakash, N., Shen, J., Moganty, S. S., Corona, A., Archer, L. A. Porous Hollow Carbon@Sulfur Composites for High-Power Lithium–Sulfur Batteries. *Angew. Chem. Int. Ed.* **2011**, *50*, 5904-5908.
[180] Yuan, Z., Peng, H.-J., Hou, T.-Z., Huang, J.-Q., Chen, C.-M., Wang, D.-W., Cheng, X.-B., Wei, F., Zhang, Q. Powering Lithium–Sulfur Battery Performance by Propelling Polysulfide Redox at Sulfiphilic Hosts. *Nano Letters* **2016**, *16*, 519-527.
[181] Mas-Ballesté, R., Guijarro, A., González-Prieto, R., Castillo, Ó., Sanz Miguel, P. J., Zamora, F. S-S Bond Reactivity in Metal-Perthiocarboxylato Compounds. *Dalton Trans.* **2010**, *39*, 1511-1518.
[182] Yu, S.-B., Holm, R. H. Tetrahedral and Square-pyramidal Sulphur-rich Complexes of Manganese(II). *Polyhedron* **1993**, *12*, 263-266.
[183] Zigler, D. F., Tordin, E., Wu, G., Iretskii, A., Cariati, E., Ford, P. C. Mononuclear Copper(I) Complexes of O-*t*-butyl-1,1-dithiooxalate and of O-*t*-butyl-1-perthio-1-thiooxalate. *Inorg. Chim. Acta* **2011**, *374*, 261-268.
[184] McConnachie, C. A., Stiefel, E. I. Ligand and Tetrathiometalate Effects in Induced Internal Electron Transfer Reactions. *Inorg. Chem.* **1999**, *38*, 964-972.
[185] Heinrich, D. D., Fackler, J. P. Synthesis and Structure of $[Au(CH_2)2PPh_2]_2[SSC(NPh)(NHPh)]_2$,a Gold(II) Ylide Dimer Containing the First Example of a Sulphur-Rich Thiourea. *J. Chem. Soc., Chem. Commun.* **1987**, 1260-1262.
[186] Kanney, J., Noll, B. C., Rakowski DuBois, M. Reactions of Thiiranes and a Thietane with a High Valent Metal Chloride. *Organometallics* **2000**, *19*, 4925-4928.
[187] Hong, M., Cao, R., Kawaguchi, H., Tatsumi, K. Synthesis and Reactions of Group 6 Metal Half-Sandwich Complexes of 2,2-Dicyanoethylene-1,1-dichalcogenolates $[(Cp^*)M\{E_2CC(CN)_2\}_2]^-$ (M = Mo, W; E = S, Se). *Inorg. Chem.* **2002**, *41*, 4824-4833.
[188] Belaj, F., Dupe, A., Mösch-Zanetti, N. C. *CSD Communication* **2022**.
[189] Sousa-Pedrares, A., Durán-Carril, M. L., Romero, J., García-Vázquez, J. A., Sousa, A. Synthesis and Characterization of Homoleptic Chromium(III) Complexes Containing Pyridine-2-thionato Ligands and of the Co-crystal (1:1) Bis(pyridine-2-thionato)(pyridine-2-dithionato) Chromium(III) Tris(pyridine-2-thionato) Chromium(III). *Polyhedron* **2013**, *62*, 278-285.
[190] Zhu, H.-B., Wu, Y.-F., Zhao, Y., Hu, J. Unprecedented Metal-mediated in situ Reactions of Heterocyclic Disulfide of Di[4-(pyridin-2-yl)pyrimidinyl]disulfide. *Dalton Trans.* **2014**, *43*, 17156-17162.
[191] Ganguly, T., Majumdar, A. Comparative Study for the Cobalt(II)- and Iron(II)-Mediated Desulfurization of Disulfides Demonstrating That the C–S Bond Cleavage Step Precedes the S–S Bond Cleavage Step. *Inorg. Chem.* **2020**, *59*, 4037-4048.
[192] Schuerman, J. A., Fronczek, F. R., Selbin, J. Crystal and Molecular Structures of Tetranuclear Metal Clusters of Copper(I) Trithioperoxybenzoates. *Inorg. Chim. Acta* **1988**, *148*, 177-183.
[193] Rombach, M., Vahrenkamp, H. Pyrazolylborate−Zinc−Hydrosulfide Complexes and Their Reactions. *Inorg. Chem.* **2001**, *40*, 6144-6150.
[194] Pan, W. H., Harmer, M. A., Halbert, T. R., Stiefel, E. I. Induced Internal Redox Processes in Molybdenum-Sulfur Chemistry: Conversion of MOS_4^{2-} to $Mo_2S_8^{2-}$ by Organic Disulfides. *J. Am. Chem. Soc.* **1984**, *106*, 459-460.

Table 1. Structurally characterized metal disulfanido complexes categorized by ligand substituent with selected parameters.

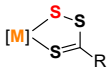
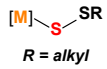
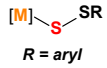
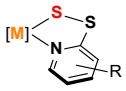
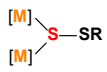
	M	Bond Distances (Å)	Bond Angles (°)	Ref.
	Mn, Co, Ni, Cu, Zn, Mo, Tc, W, Re, Pt	M–S: 2.122(2) – 2.506 S–S: 1.985(3) – 2.124(3) S–C: 1.60(2) – 1.84(2)	M–S–S: 95.85 – 111.42 S–S–C: 103.66 – 112.94	[101, 181-185]
	Ti, Cu, Zn, Mo, Ru, W, Re, Pt, Au	M–S: 2.221(2) – 2.4379 S–S: 2.02(1) – 2.140(3) S–C: 1.718(7) – 1.878(1)	M–S–S: 92.35 – 114.12 S–S–C: 96.25 – 109.16	[109, 139, 146, 186-187]
	W	M–S: 2.5062 S–S: 2.0533 S–C: 1.7560	M–S–S: 113.32 S–S–C: 104.16	[145]
	Cr, Fe, Co, Mo, W	M–S: 2.179(1) – 2.387(1) S–S: 2.040(2) – 2.107(3) S–C: 1.701(6) – 1.76(1)	M–S–S: 96.71 – 103.08 S–S–C: 100.41 – 102.71	[148, 188-190]
	Cr, Mn, Fe, Ni, Cu, Mo, Re, Os	M–S: 2.202(2) – 2.668(2) S–S: 2.011(4) – 2.225(3) S–C: 1.657 – 1.847(8)	M–S–S: 98.08 – 116.28 S–S–C: 96.77 – 109.46	[124, 132, 134, 191-192]

Table 2. Structurally characterized metal polysulfanido complexes with selected parameters.

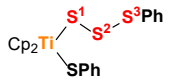
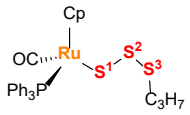
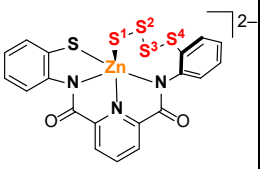
	Bond Distances (Å)	Bond Angles (°)	Ref.
	Ti–S^1: 2.439(3) S^1–S^2: 2.053(3) S^2–S^3: 2.011(3) S^3–C: 1.756(8)	Ti–S^1–S^2: 115.48 S^1–S^2–S^3: 109.26 S^2–S^3–C: 106.74	[103]
	Ti–S^1: 2.470(3) Ti–S^2: 2.545(3) S^1–S^2: 2.028(3) S^2–S^3: 2.084(3) S^3–C: 1.831(9)	Ti–S^1–S^2: 68.09 Ti–S^2–S^1: 64.22 Ti–S^2–S^3: 111.22 S^1–S^2–S^3: 113.65 S^2–S^3–C: 106.72	[138]
	Ru–S^1: 2.370(3) S^1–S^2: 2.043(4) S^2–S^3: 2.005(5) S^3–C: 1.95(1)	Ru–S^1–S^2: 110.04 S^1–S^2–S^3: 109.61 S^2–S^3–C: 105.94	[140]
	Zn–S^1: 2.3900(7) S^1–S^2: 2.0370(9) S^2–S^3: 2.0561(8) S^3–S^4: 2.0587(8) S^4–C: 1.777(2)	Zn–S^1–S^2: 111.95 S^1–S^2–S^3: 110.07 S^2–S^3–S^4: 107.54 S^3–S^4–C: 103.84	[142]

Figure Captions:

Figure 1. Examples of metal-sulfur species in biology with sulfur-centered reactivity. Hydrosulfide coordination at the heme center of cytochrome P450 (left). An example of a His_2Cys_2 zinc finger site (right).

Figure 2. Scope and nomenclature of metal-sulfur complexes discussed.

Scheme 1. Synthesis of metal sulfide complexes by (A) sulfide addition or (B) reduction of S_8.

Figure 3. Coordination modes of transition metal hydrosulfido complexes.

Scheme 2. Sulfur-centered reactions of a tris(pyrazolyl)borate-supported zinc hydrosulfido complex.[193]

Scheme 3. Deprotonation of **5** forms sulfido-bridged bimetallic complex **6**.[61]

Figure 4. A μ_4-sulfido ligand has been proposed to participate in N_2O activation.[65]

Figure 5. Relative energies of valence *d* orbitals for a model metal terminal sulfido complex with C_{4v} symmetry.

Scheme 4. Synthesis and nucleophilic reactivity of a terminal zirconium sulfido complex (**9**).

Figure 6. Examples of terminal sulfido complexes of group VI metals.

Scheme 5. Tetrathioperrhenate addition to norbornene.

Figure 7. Examples of late transition metal terminal sulfido complexes.

Figure 8. Selected examples of transition metal polysulfido complexes.

Scheme 6. The thiomolybdate anion can undergo both sulfur- and molybdenum-centered redox processes.[194]

Scheme 7. Sulfur insertion to a tris(pyrazolyl)borate-supported yttrium sulfido cluster forms yttrium disulfido and pentasulfido clusters.

Scheme 8. Reduction of polysulfido complexes to hydrosulfido or sulfido species.

Scheme 9. Oxidation of nickel-bound disulfido results in formation of S_8.

Scheme 10. Synthetic routes towards metal polysulfanido complexes.

Scheme 11. Polysulfide nucleophilic attack on CS_2.

Scheme 12. Ruthenium disulfanido complex synthesis via thiolate attack on thiosulfonate ligand.

Scheme 13. Synthesis of titanium disulfanido complexes through oxidative addition across S−S or S−N bonds.

Scheme 14. Synthesis of tris(pyrazolyl)borate-supported zinc disulfanido complexes.

Scheme 15. S_8 insertion into chelating dithiocarboxylates.

Scheme 16. Diiron bridging disulfanido synthesis via disulfide attack upon thiobenzophenone.

Scheme 17. Proposed pathway for disulfanide-bridged tetracopper cluster formation.

Scheme 18. Migratory insertion of trisulfur fragment into a Ti−C bond results in a titanium trisulfanido complex.

Scheme 19. Electrophile-dependent divergence of titanium di- or trisulfanido complex formation.

Scheme 20. Titanium trisulfanido complex formation via sulfur atom migration between disulfanido ligands.

Scheme 21. Ruthenium trisulfanido complex synthesis via hydrosulfido attack upon a formal RSS^+ donor.

Scheme 22. S_8 inserts reversibly into a Zn−S(thiolate) bond to form a zinc tetrasulfanido complex.

Scheme 23. Oxidation of a zinc tetrasulfanido complex leads to a dizinc species with organotrisulfide-containing ligand, while reduction reforms **58** and releases $S_3^{\bullet -}$.

Scheme 24. Redox reactions of Mo^{IV} and W^{IV} disulfanido complexes show the interplay between metal center and disulfanide S−S bond.

Scheme 25. Interconversion of dirhenium complexes between bridging disulfido and bridging bis-disulfanido moieties.

Scheme 26. Nucleophilic reactivity of zinc tetrasulfanido complex.

Scheme 27. Perthionitrite addition to $FeCl_2$ forms sulfido-bridged and polysulfido-supported DNICs.[160]

Scheme 28. Conversion of dichromium sulfide to disulfanido complex via nitrosylation.

Scheme 29. Synthesis of zinc perthionitrite and thionitrite (both *anti* and *syn* isomers) complexes.

Scheme 30. N_2O trapping by masked terminal M^{2+} sulfide complexes forms chelating thiohyponitrite ligands.

Scheme 31. Light-mediated, reversible formation of COS from a molybdenum disulfide-CO adduct.