

Review

Metal-radical coordination complexes of thiazyl and selenazyl ligands



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ABSTRACT

The so-called “metal-radical approach” to the design of molecule-based magnetic materials relies on the availability of paramagnetic ligands that can reliably form coordination complexes with paramagnetic metal ions. While the most common radical ligands are based on nitroxides, other paramagnetic building blocks are also gaining attention. Thiazyls and their related selenazyls are promising candidates for the development of radical ligands and, because they have inherently interesting materials’ properties, their use as ligands has the potential to generate novel materials with unprecedented properties. Significant progress has been made in this field in the past ten years. This review is a timely look back at the development of the field, highlighting the diversity of complexes and designs, and a look forward to a promising future.

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1. Introduction

Thiazyls are an interesting class of compound that contain the unsaturated, odd-electron S=N linkage. The documented study of thiazyls dates back at least as far as 1835, to the preparation of S_4N_4 from the reaction of sulfur monochloride with ammonia

[1]. Although S_4N_4 is shock-sensitive and can detonate to generate elemental sulfur and nitrogen, controlled decomposition of S_4N_4 generates poly(sulfur nitride), $(SN)_x$, a fascinating bronze colored material [2] that exhibits metallic [3] and superconducting [4] properties. Thus, in only a few steps from very basic reagents, a thiazyl compound with impressive materials’ properties can be prepared.

With renewed interest in $(SN)_x$ in the 1970s came a renaissance in thiazyl chemistry [5]. In particular, the propensity of thiazyls to form isolable paramagnetic species [6] drew attention from

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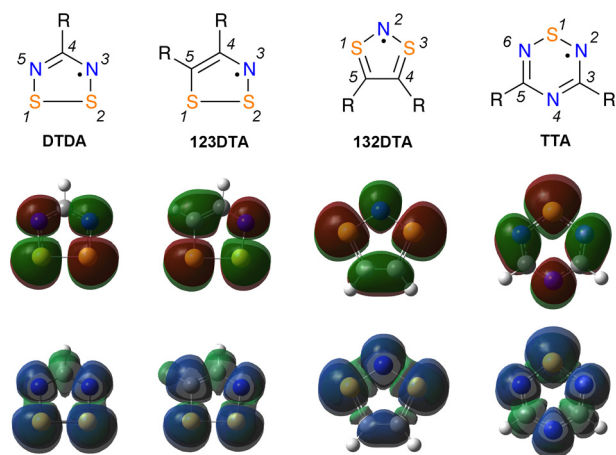


Fig. 1. Generic structures and numbering schemes for the neutral thiazyl heterocycles discussed herein; surfaces of singly occupied molecular orbitals (SOMOs) and total Mulliken spin density (blue = α ; green = β) for the thiazyls ($R=H$), generated from DFT calculations using b3lyp/6-31G(d,p) [25] and rendered using isovalues of 0.020000 for the MOs and 0.000400 for densities [26]. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

theoreticians and synthetic chemists alike. A diverse variety of paramagnetic thiazyl heterocycles can be prepared and stored as pure materials for prolonged periods. The caveat is that many thiazyl species are susceptible to hydrolysis and/or reaction with atmospheric oxygen [7–9], thus inert atmosphere and anhydrous reaction/storage conditions may be required. In the last fifty years, an extensive body of work has been developed, with ever more challenging designs and synthetic methodologies, and ever more exciting materials' properties reported. Examples of the wide range of impressive properties exhibited by thiazyl-based molecular materials include magnetic ordering as a spin-canted antiferromagnet at 36 K [10], ferromagnetic ordering at 1.32 K [11], magnetic bistability with a large hysteresis centered around room temperature [12], and metallic conductivity under pressure [13]. By incorporating selenium in the place of sulfur, making structurally analogous selenazyl and thiaselenazyl molecular materials, improved and altered materials' properties have been reported, including ferromagnetic ordering temperatures as high as 17.5 K [14] and hysteretic spin-crossover [15].

A key structural feature of most thiazyl radicals, strongly correlated to the resulting materials' properties, is the high spin density at S and N atoms that are devoid of substituents (Fig. 1). These heteroatoms are free to engage in supramolecular contacts, directing the crystal packing in the solid structure and providing the primary pathways for magnetic and conductive properties. They are also free to participate in chemical reactions, such as hydrolysis [7,16] and oxidation with O_2 [9,17]. Thus, the structural features that give rise to the most interesting and technologically promising properties of thiazyl radicals are the same features that impart air-sensitivity, which can make working with these species somewhat challenging. It should be noted, however, that some of the more recently designed paramagnetic thiazyls are air-stable [18,19], a welcome advancement in this field. In addition, the network of intermolecular interactions that gives rise to supramolecular materials' properties also contributes to the lattice enthalpy in the solid state, decreasing the solubility and volatility of these species, a second challenge which may be overcome by judicious choice of solvent or solvent mixtures and molecular design.

Although the reactivity of many thiazyls can be a disadvantage, it is this very feature that may also be of interest. Apart from hydrolysis and oxidation, reactivity with other reagents such as atomic nitrogen [20] and metal-containing species (*vide infra*) have been

reported. The present review is primarily concerned with the latter, the reactivity of thiazyl and selenazyl radicals with metal-based reagents and the resulting coordination complexes.

Reasons for exploring the reactivity of thiazyl and selenazyl radicals with metal-based reagents can be roughly divided into two categories: (1) elucidation of the nature and reactivity of this interesting family of paramagnetic compounds and (2) development of paramagnetic ligands that will remain intact upon coordination, generating novel molecular materials with enhanced or unprecedented properties. The former is primarily concerned with the chemistry of thiazyl ring systems, viewing them as a synthetic precursor with the potential to contribute to therapeutic, pharmaceutical or pesticide related applications. Low valent metal components (0 or +1 oxidation states) are typically employed and reaction occurs at the S atoms. In some cases, the heterocycles remain intact, but it is also common for bonds to be broken, possibly with the abstraction of atoms from the system. The latter approach seeks to advance the so-called “metal-radical approach” [21] to molecular materials design by exploiting the unique intermolecular interactions available with thiazyl species, thereby adding another facet to the electronic and magnetic properties. Thus, the real advantage of thiazyl-based ligands compared to other paramagnetic ligands lies in the potential for intermolecular interactions. The N atoms are viewed as σ -donor coordination sites and harder metal ions (+2 or +3 oxidation state) are typically employed. Ultimately, both approaches have generated valuable insight.

As recently as ten years ago, metal-thiazyl coordination chemistry was still in its infancy and progress in the area was documented in a limited number of reviews [22–24]. The past decade has witnessed acceleration in the growth and progress of this field, with increased diversity in designs and results. This is a good time to take stock of what has been achieved and look forward to the future. With this in mind, the present review is a timely overview of the field and its current status with the hope that new directions will be encouraged and that the next decade is as exciting as the past ten years have been.

2. Complexes of 1,2,3,5-dithiadiazolyl (DTDA) and 1,2,3,5-diselenadiazolyl (DSDA)

The 1,2,3,5-dithiadiazolyl (DTDA) heterocycles and their selenium analogs (DSDA) are arguably the most intensely and thoroughly studied paramagnetic thiazyls. This is, in part, due to valuable and reliable synthetic methodologies that have made it possible to synthesize **RDTDA** species with a wide range of R substituents (Fig. 1) [27–33]. As such, it is not surprising that DTDA were the first class of thiazyl radical to be investigated with respect to metal coordination (*vide infra*) as well as the species for which the largest number of metal-thiazyl coordination complexes having been reported to date.

2.1. S-coordination complexes

In 1989, Banister et al. reported the first metal coordination complex of a DTDA, prepared by reacting **PhDTDA** with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ [34]. The product of these reactions was originally assigned as $Fe_2(CO)_6(PhCN_2S_2)$, wherein $(CO)_3Fe-Fe(CO)_3$ is inserted into the S–S bond of the **PhDTDA** radical. It was later discovered that the orange product is actually the related diamagnetic imine **$Fe_2(CO)_6PhDTDAH$** (Fig. 2), bearing a hydrogen atom at one of the thiazyl N sites [22,35,36]. Reports of reactions between **PhDTDA** and a variety of other low valent metal precursors soon followed, illustrating a diverse series of S-coordination motifs. The **$Ni_2Cp_2PhDTDA$** complex is structurally analogous to the original di-iron complex, and the species remains paramagnetic

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