



# Thermal, optical and structural properties of disulfide and diselenide salts with weakly associated anions



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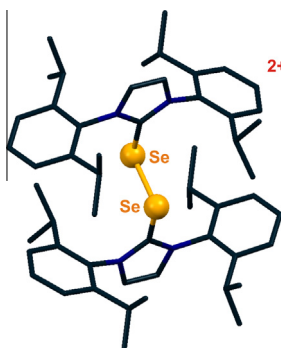
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## HIGHLIGHTS

- Imidazole disulfide and diselenide salts were synthesized using metal salts as oxidants.
- First Bi(OTf)<sub>3</sub> mediated oxidation of IPrS and IPrSe was reported.
- First perchlorate salt of diselenide cation was isolated.
- Strong intermolecular hydrogen bonding along with E···O weak interactions were observed for disulfide and diselenide salts.
- Thermal and optical properties of disulfide and diselenide salts were studied.

## GRAPHICAL ABSTRACT

Syntheses, structural and thermal properties of imidazole disulfide and diselenide dications with weakly associated anions were discussed.



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## ABSTRACT

The imidazole disulfide and diselenide dications were conveniently isolated for the first time by treating imidazole thione or imidazole selone with bismuth(III) triflate or copper perchlorate hexa-hydrate in very good yield. These new salts were characterized by elemental analysis, FT-IR, solid state UV–vis, thermogravimetric analysis and single crystal X-ray diffraction techniques. Interesting thermal properties and unusual bonding situations were observed for these dichalcogenide salts.

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## Introduction

Oxidation of 1,3-disubstituted imidazole thione or selone has proven to be pivotal reaction for a variety of biological and material processes. Such transformations afford formally 1,3-disubstituted imidazole disulfide dication or diselenide dication with anionic

ligands capable of balancing the charge. Notably, the anions play a crucial role in the biological and material processes. It has been well documented that the 1,3-disubstituted imidazole thione or selone can be conveniently oxidized by Te, ICl, IBr [1,2], 7,7,8,8-tetracyano-p-quinodimethane [2], I<sub>2</sub> [3,4], HCl/air [5–7] and Br<sub>2</sub> [8–10]. Thus, a variety of 1,3-disubstituted imidazole disulfide dication or diselenide dication have been generated and some are structurally characterized. However despite the growing number of examples documenting their chemical reactivity, the oxidation

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of 1,3-disubstituted imidazole thione or selone under metal salt route has not been realized until 2012. The first triflate salts of 1,3-disubstituted imidazole disulfide dications or diselenide dications have been derived using  $\text{Cu}(\text{OTf})_2$  [11], while similar such reactions are not reported with other metal salts. With the intention of verifying the ability of metal salts in the above process, we investigated the oxidative reactions of sterically crowded IPrE or IPr'E with  $\text{Bi}(\text{OTf})_3$  or  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  for the first time.

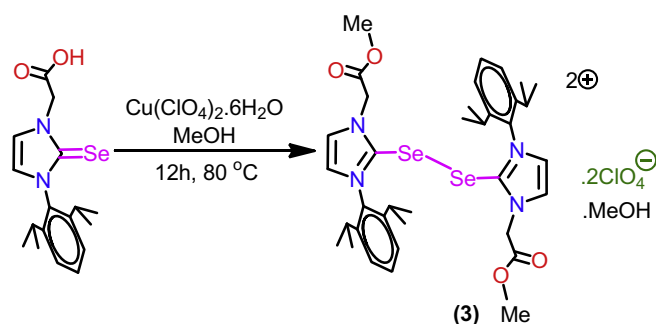
## Results and discussions

### Synthesis and structural characterization

In contrast to the known synthetic routes [1–11], in this paper we report a novel bismuth triflate mediated oxidation of IPrE (E = S or Se) to isolate the first bistriflate salts of  $[\text{IPrS}(\text{OTf})_2]_2$  (**1**) and  $[\text{IPrSe}(\text{OTf})_2]_2$  (**2**) (Scheme 1).

Similarly, ester functionalized perchlorate salt of diselenide  $[\text{IPr}'\text{Se}(\text{ClO}_4)]_2 \cdot \text{MeOH}$  (**3**) was isolated by treating carboxylic acid functionalized IPr'Se with copper perchlorate hexa-hydrate in methanol (Scheme 2). Whereas, attempts to synthesis ester functionalized perchlorate salt of disulfide  $[\text{IPr}'\text{S}(\text{ClO}_4)]_2$  using copper perchlorate hexa-hydrate in methanol or  $[\text{IPr}'\text{S}(\text{ClO}_4)]_2$  by  $\text{Bi}(\text{OTf})_3$  in toluene were not successful. Compounds **1–3** are insoluble in common solvents. Thus these salts were characterized by elemental analysis, FT-IR, thermogravimetric analysis and solid state UV-vis. The presence of uncoordinated triflate anions in **1** and **2** are confirmed by corresponding stretching frequency observed at  $1388$  (for **1**) and  $1387$   $\text{cm}^{-1}$  (for **2**). The FT-IR spectrum of **3** showed a sharp signal at  $1068$   $\text{cm}^{-1}$  for the uncoordinated perchlorate anions and the strong peaks at  $1750$  and  $1200$   $\text{cm}^{-1}$  for the presence of ester groups.

The solid state structures of **1–3** were unambiguously determined by single crystal X-ray diffraction technique. The suitable single crystals of **1** and **2** for the X-ray analysis were obtained from the saturated solutions of acetonitrile, layered with *n*-hexane at room temperature. The single crystals of **3** for the X-ray analysis were isolated from its reaction mixture. **1** and **2** crystallized in the triclinic space group,  $P\bar{1}$  with two triflate ions, while **3** crystallized in the orthorhombic space group,  $P2_12_12_1$  with two perchlorate anions and one methanol molecule [14,15]. Molecular structures of **1–3** are depicted in Fig. 1. The crystallographic data for **1–3** are provided in Table 1 and the significant bond parameters are listed in Table 2. Molecules **1–3** are isostructural, thus the structural features of **1–3** are not discussed individually. In **1–3**, the dichalcogenide fragment E–E is tethered by two imidazole ligands. The imidazole moieties in **1–3** are arranged in *trans* position. The S–S bond length in **1** is  $2.1701(15)$  Å is slightly longer than the previously reported disulfide



Scheme 2. Synthesis of **3**.

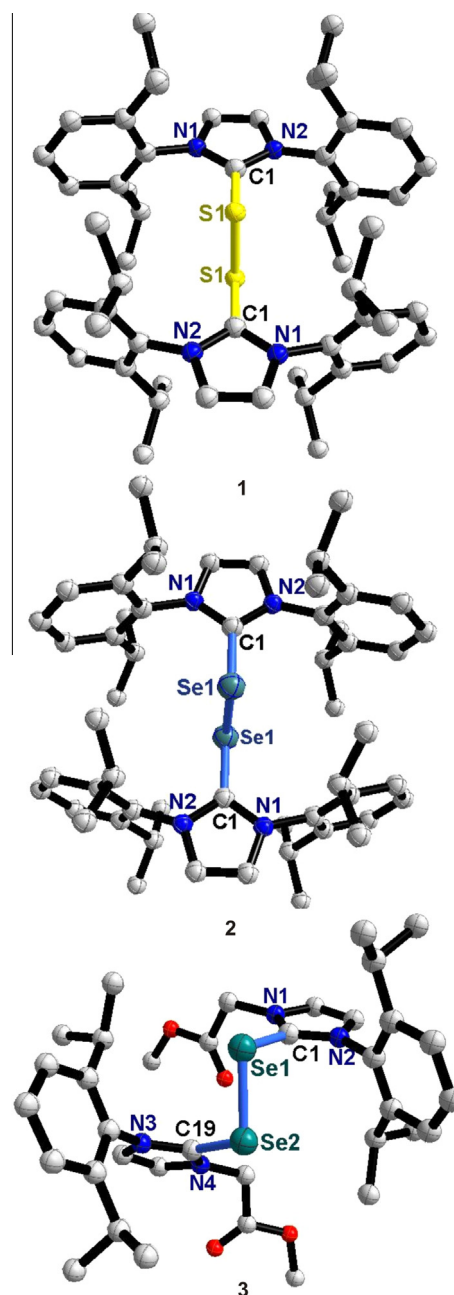
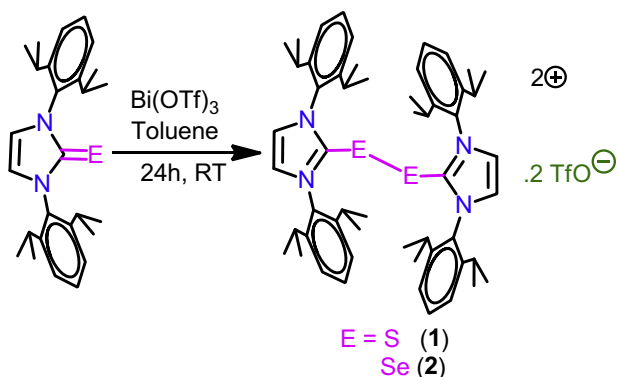


Fig. 1. Molecular structures of **1–3**. Hydrogen atoms and triflate anions have been omitted for clarity in **1** and **2**. Hydrogen atoms, perchlorate anions and methanol have been omitted for clarity in **3**.



Scheme 1. Synthesis of **1** and **2**.

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