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Remarkably Stable Chalcogen(II) Dications

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The diiminopyridine ligand (DIMPY) has become an omnipresent ligand in transition-metal chemistry, as it can stabilize reactive metal centers that have shown great utility in catalysis.[1] Analogous neutral or monocationic p-block derivatives from groups 13−15 have been reported, although often with only a few or singular representatives, except in the cases of tin and lead, where a plethora of compounds have been identified (**1**; Figure 1).[2] Nonmetal as well as dicationic congeners have remained decidedly elusive. These highly charged species are of interest, as they possess atom centers that are potentially powerful reagents for a variety of stoichiometric or catalytic reactions.[3]

In this context, we report the synthesis and characterization of the first *N*,*N*′,*N*″-DIMPY coordination complexes (**1S**, **1Se**, **1Te**) for the chalcogens. This homologous series features formally dicationic chalcogen centers, with the sulfur derivative as the single example of a nonmetal DIMPY complex. Furthermore, all three are remarkably stable under open atmosphere, in distinction from their α-diimine relatives, which offers the opportunity to exploit the chemical utility of these highly unusual species.[3f,g]

The 1:1 stochiometric reaction of a $Ch(OTf)_2$ (Ch = S, Se, Te) synthon with R_2DIMPY [R = 2,6-diisopropylphenyl (Dipp); R = 2,6-dimethylphenyl (Dmp) for **1bTe**] at room temperature or −78 °C (**1S**) resulted in the immediate precipitation of solid material (Scheme 1). The supernatant was decanted from **1Se** and **1Te**, and the powders were washed with Et_2O. The resulting solids were dried in vacuo to give yellow/amber powders. For compound **1S**, the solvent was removed in vacuo, and the solids were recrystallized from an acetonitrile/ether solution. Samples of the bulk material were redissolved in acetonitrile-d_3 for multinuclear NMR spectroscopy.

The ^1H NMR spectra displayed significantly downfield resonances for the protons resident on the α-carbon and were diagnostic for a dicationic complex [**1S**, 10.36 ppm; **1Se**, 10.35 ppm; **1aTe**, 10.53 ppm; **1bTe**, 10.47 ppm (cf. $Dipp_2$DIMPY, 8.44 ppm; Dmp_2DIMPY, 8.43 ppm)].[4] All of the spectra indicated a single product with a symmetric environment for the DIMPY ligand, contrary to the report of a chalcogen−DIMPY system that resulted in an N,N′,C-bound tellurium center.[5] The $^{19}F\{^1H\}$ NMR spectrum was indicative of ionic triflate in solution for all of the complexes, indicating minimal cation−anion association in solution [**1S**, −78.5 ppm; **1Se**, −78.5 ppm; **1aTe**, −78.6 ppm; **1bTe**, −78.7 ppm (cf. ionic $[NOct_4][OTf]$, −78.5 ppm; covalent CH_3OTf, −75.4 ppm)].[6] Crystals of **1S**, **1Se**, and **1bTe** suitable for X-ray diffraction studies were grown by vapor diffusion of Et_2O into acetonitrile solutions of the redissolved bulk powders. In all cases, the diffraction experiments revealed dicationic complexes of the respective chalcogen, where the salts were isolated in high yields (**1S**, 82%; **1Se**, 87%; **1bTe**, 90%) (Figure 2). Despite valiant efforts, suitable crystals of **1aTe** could not be obtained; however, the bulk material was comprehensively characterized, and all of the data were consistent with the proposed formulation, which was obtained in 99% yield.

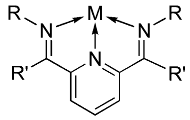
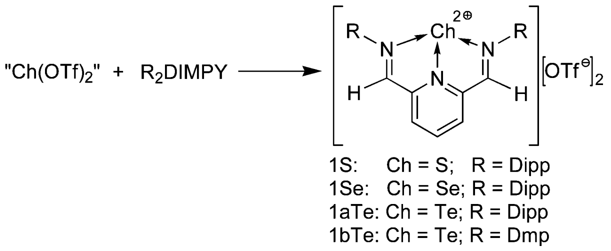


Figure 1. General structure for a metal DIMPY complex (**1**).

Scheme 1. Synthetic Routes to **1S**, **1Se**, **1aTe**, and **1bTe**



Compounds **1S**, **1Se**, and **1bTe** exhibit a T-shaped geometry about the chalcogen center, consistent with an AX_3E_2 electron pair configuration. Both of the imine nitrogen atoms occupy axial positions within the trigonal bipyramid, and the pyridine nitrogen and the two lone pairs occupy the equatorial positions. For **1S**, the N(2)−S(1) bond is slightly shorter than typical N−S single bonds [1.719(3) Å (cf. 1.76 Å)] and slightly longer than in the only other known sulfur(II) dicationic systems [1.655(3)−1.699(6) Å], which can be attributed to the increase in coordination number from 2 to 3.[3f,7] The N(1/1A)−S(1) bonds are considerably longer [1.9068(17) Å], which is likely a consequence of having two nitrogen atoms donate into the unhybridized p orbital. A positive correlation is observed between increasing size of the central atom and increasing Ch−N bond lengths for **1S**, **1Se**, and **1bTe**. In all of the compounds, the axial Ch−N(1/1A/3) bonds are longer than the equatorial Ch−N(2) bonds [Se−N(1/1A), 2.025(2) Å; Se−N(2), 1.872(3) Å; Te−N(1)/N(3), 2.243(4) Å; Te−N(2), 2.098(3) Å]. There are no detectable cation−anion contacts within the sum of the van der Waals radii between the triflate anion and the chalcogen center in **1S** or in **1Se** (S···O, 3.25 Å; Se···O, 3.42 Å), but **1bTe** displays distant Te···O contacts within the sum of the van der Waals radii [closest contact 2.776(4) Å (cf. 3.58 Å)].[7] Upon close inspection of the tellurium structure, the corresponding sulfur oxygen bond lengths within the anion show no asymmetry, consistent with the absence of a covalent interaction between the dicationic chalcogen center and the anion. The dative bonding model is drawn in Scheme 1, but in view of the metrical parameters, the charge is likely delocalized throughout the dication, resulting in a hybrid structure best represented as the pyridinium/iminium salt.

Much to our surprise, storing the samples under open air led to no signs of decomposition for a period of three weeks for **1Se** and 2 months for **1S** and **1Te**, in stark contrast to the highly unstable monodentate and bidentate dicationic derivatives.[3f,g,8] Even after the addition of water to **1S**, no decomposition was observed over

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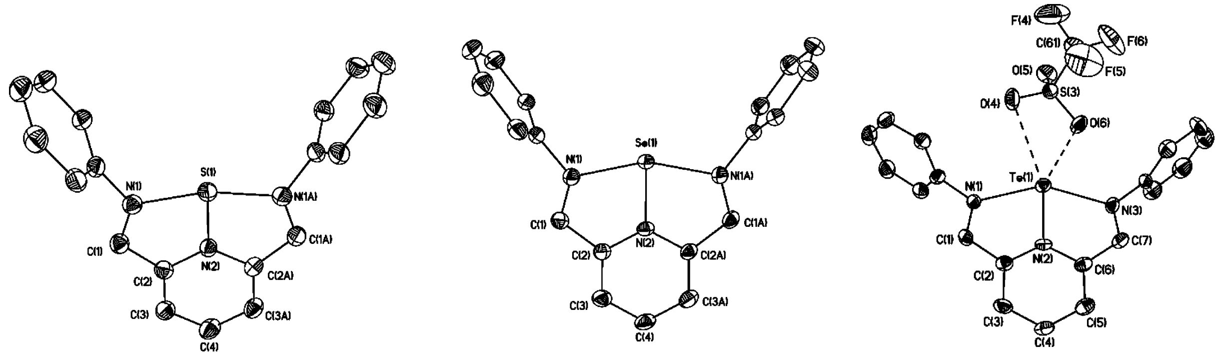

1S **1Se** **1bTe**

Figure 2. Solid-state structures of the cations **1S**·Et$_2$O, **1Se**·Et$_2$O, and **1bTe**·CH$_3$CN. Ellipsoids are drawn to the 50% probability level. Hydrogen atoms, isopropyl or methyl groups, solvates, and anions not interacting with the chalcogen center have been omitted for clarity. Selected bond lengths (Å) for **1S**: S(1)−N(1/1A), 1.9068(17); S(1)−N(2), 1.719(3). For **1Se**: Se(1)−N(1/1A), 2.025(2); Se(1)−N(2), 1.872(3). For **1bTe**: Te(1)−N(1), 2.243(4); Te(1)−N(2), 2.098(3); Te(1)−N(3), 2.243(4); Te(1)···O(4), 3.060(5); Te(1)···O(6), 2.776(4).

1 h, a remarkable feature for such species. However, compounds **1Se** and **1Te** decomposed immediately upon the addition of water.

In summary, by the metathesis reactions of chalcogen bis(triflate) synthons with DIMPY ligands, the corresponding complexes were synthesized and structurally characterized. These species are particularly stable, an unusual feature of highly charged dications, and we are currently investigating their reactivity.

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Supporting Information Available: Experimental details, full characterization data, and crystallographic data for **1S**, **1Se**, and **1bTe** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The stability of the complexes was confirmed by ^{1}H NMR spectroscopy. The spectra are given in the Supporting Information.

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