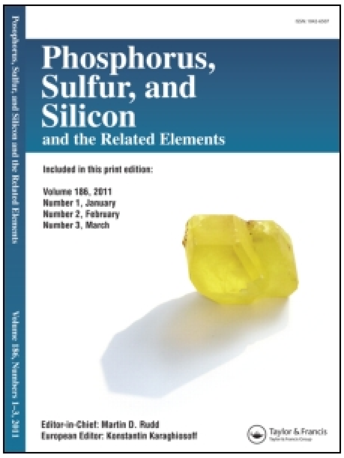

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Materials Chemistry of 1,2,3-Selenadiazoles

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Materials Chemistry of 1,2,3-Selenadiazoles

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The organic chemistry of 1,2,3-selenadiazoles has been explored to a greater extent due to the fact that the chemistry of 1,2,3-selenadiazoles mostly is driven by its facile decomposition via elimination of a nitrogen molecule and formation of selenaketocarben and/or its dimerization to 1,4-diselenin. The reactions of 1,2,3-selenadiazoles directly with various transition metal compounds have resulted in unique organo-selenium transition metal complexes. However, the materials chemistry of 1,2,3-selenadiazoles has not appeared in literature prior to the first publication on the subject from our laboratory in 2003. To, the best of our knowledge, no research group is engaged in such an activity. We, have exclusively explored the potential of 1,2,3-selenadiazoles for their effective utilization in synthesis of semiconductor nano particles or nano powder and in this lecture, the results and methodology for the same would be discussed.

Keywords 1,2,3-selenadiazoles; CdSe; EDAX

INTRODUCTION

Since the first synthesis of 1,2,3-selenadiazoles in 1970,[1,2] its chemistry is much less explored in the past three decades. In the early years of research on 1,2,3-selenadiazoles, focus mainly was centered around the organic synthesis.[3] Later, organo-transition metal complexes were synthesized from the reaction of alkeno-1,2,3-selenadiazoles with transition metal complexes.[4–9] Formation of 1,4-diselenine in these reactions also has been observed and the reactivity of that with Pd(II) and

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Pt(II)[4,5] also has been described in the literature. In addition, there also are a few reports on charge-transfer complexes of selenium donors derived from 1,2,3-selenadiazoles.[10,11] Thermal decomposition of 1,2,3-selenadiazoles has been described in the past.[12] The ability to release free elemental selenium has been mainly utilized in organic synthesis to prepare alkynes.[16] Recently[18] it has been reported that a series of 1,2,3-selenadiazoles, when treated with olefins, yielded dihydroselenophenenes along with 1,4-diselenins and selenophenes as byproducts when cyclohexeno-1,2,3-selenadiazole was heated to 130°C for 15 h without olefins. Corresponding 1,4-diselenin was formed in more than 80% yield. We exclusively have tested the suitability of cycloocteno-1,2,3-selenadiazoles as source of free selenium with various transition metals[17–20] and in the process, we have discovered an improved and efficient synthesis of bis(cycloocteno)-1,4-diselenin. In the present article, it is attempted briefly to highlight some of the work carried out in our laboratory related to materials chemistry of alkeno-1,2,3-selenadiazoles.

EXPERIMENTAL SECTION

Thermolysis of 1,2,3-Selenadiazole with Metal Salts (ME; M=Cd, Ag; E=Se)[17–20]

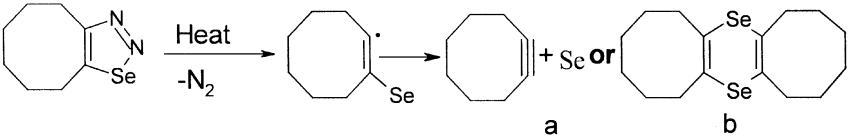
A round bottom Schlenk flask was evacuated twice and refilled with nitrogen gas. This was assembled with a condenser, nitrogen inlet and outlet. The flask was charged with selenium source (cycloalkeno-1,2,3-selenadiazole, or selenium powder) in desired solvents and respective metal salts were reacted in 1:1 ratio under nitrogen. The reaction mixture was heated for 3–5 h between 110–140°C to obtain a brownish-black suspension. This was filtered, washed with solvent of reaction, and water followed by alcohol and was dried to afford powders of desired metal selenides in good yield.

Thermolysis of 1,2,3-Selenadiazole without Metal Salts

Cycloocteno-1,2,3-selenadiazole was heated in various high boiling solvents at about 120°C under nitrogen atmosphere in a round bottom Schlenk flask with constant stirring for a few hours (typically 3–5 hrs). Upon cooling the reaction mixture to room temperature, crystalline yellow precipitate was filtered and washed with light petroleum ether to collect bis(octeno)-1,4-diselin. Reaction of tetracyanoquino dimethane (TCNQ) with diselenin in acetonitrile at boiling temperature resulted in formation of black shiny powder.

RESULTS AND DISCUSSION

Thermal decomposition of 1,2,3-selenadiazoles has been described to proceed either via formation of an intermediate selenaketocarbene which further proceeds via elimination of selenium or via the formation of a dimerized compound, 1,4-diselenin (Scheme 1) and both these reactions have been studied widely.[12]



SCHEME 1 Thermal decomposition of cycloocteno-1,2,3-selenadiazole.

The reaction of metal salts with *in-situ* released selenium resulted in formation of respective metal selenides possibly due to reduction of metal salts by ethylene glycol. We have carried out experiments involving cadmium and silver metal salts to prepare CdSe and Ag_2Se. The scanning electron micrograph (Figure 1) shows that the diameter of the particles is well below 500 nm and that they are of similar quality when compared to the powder that is obtained from the selanadiazole experiment. The confirmation of the presence of stoichiometric cadmiun and selenium was done by EDAX analysis. The powder X-ray diffraction pattern (Figure (2a)) shows hexagonal phases of CdSe with slight impurities of selenium and solid state absorption spectrum of the product is shown in Figure 2(b).

It was observed that when no cadmium chloride is added to selenadiazole, the intermediate selenoketocarbene, dimerizes to produce compound (**b**) (Scheme 1) thus taking a different reaction path and may be similar to what is already reported for such a conversion.

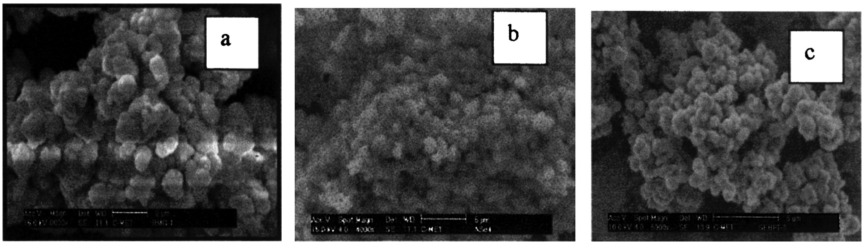


FIGURE 1 Scanning electron micrograms of CdSe (a) from Octeno-1,2,3-selenadiazole in EG, and Ag_2Se (b) & CdSe (c) from Hepteno-1,2,3-selenadiazoles in EG (reproduced with permission from Elsevier publication ref. No. [14, 15, 17].)

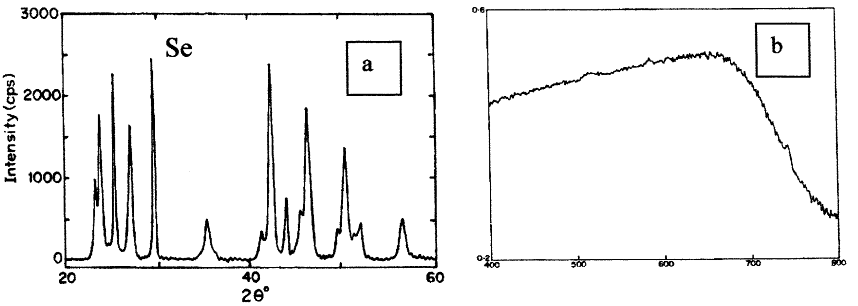


FIGURE 2 (a) XRD pattern and (b) solid state UV-Visible spectrum of CdSe powder (Reproduced with permission from Elsevier publication ref. No. [14].).

However, during the presence of cadmium metal salt, released free-elemental selenium combines with the cadmium ion to produce CdSe when the experiment was carried out in dimethylformamide (DMF). Thus compound **(b)** as per Scheme 1 was synthesized by a modified method via thermolysis of cycloocteno-1,2,3-selendaiazole in ethylene glycol at about 120°C at normal pressure under an inert atmosphere of dry nitrogen gas, as a yellow crystalline product melting at about 145°C. It was observed in its proton and carbon NMR and in all other analyses that data matched well with the reported values. The mass spectrum of the product prepared from the current method revealed a molecular ion peak (m/z) at 374 with typical fragmentation pattern for selenium compound containing ^{80}Se isotopes. Attempts were made to generate charge-transfer complexes from the reaction of 1,2,3-selenadiazole and 1,4-diselenin with TCNQ but these resulted in formation only of a black crystalline solids with varied spectroscopic observations. An absorption spectrum of the black solution showed a new absorption band positioned at 478 and it is considered to be due to the charge-transfer from the Se-donor to pi-acceptor molecule. Further work on this aspect is in progress to establish the authenticity.

CONCLUSION

The reactions involving cadmium and silver metal salts with cycloocteno- and hepteno-1,2,3-selenadiazoles have resulted in respective metal selenide powders that are characterized by various analytical tools. Thee methods indicated that there is a possibility of generating nanoparticles of these semiconductors for various electronic and opto-elecronic applications. The attempt to prepare charge-transfer complexes of 1,4-diselenin with TCNQ resulted in formation of a black shiny powder.

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