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SULFUR AND SELENIUM COMPOUNDS OF MAIN GROUP ELEMENTS WITH RING AND CAGE STRUCTURES

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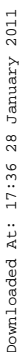
Tetraphenylphosponium polysulfides and polyselenides react with halides or halo complexes, yielding cyclic or polycyclic polysulfido and polyselenido complexes. Several compounds of phosphorous, arsenic, antimony, silicon, tin, and tellurium are presented.

Key words: polysulfido complexes; polyselenido complexes

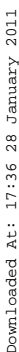
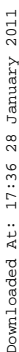
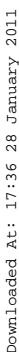
PREPARATIONS AND STRUCTURES

Polychalcogeno compounds have attracted much attention in the past years, see, for instance, the reviews ^[1-5]. We have contributed, together with many other research groups, to this development.

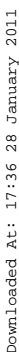
By the reaction of PPh_4Cl or PPh_4Br with Na_2S_4 or Na_2Se_4 , solutions of tetraphenylphosponium polysulfides or polyselenides can be obtained in dichloromethane or acetonitrile. The solutions contain S_x^{2-} or Se_x^{2-} ions with varying values of x being in equilibrium with each other. These solutions react readily with metal and nonmetal halides, halo complexes or even with pure elements, yielding thio-halo, polysulfido, or polyselenido complexes. From $\text{As}_2\text{X}_8^{2-}$ the ions As_2SX_5^- and $\text{As}_2\text{SX}_6^{2-}$ can be obtained ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The same products had been produced previously from arsenic sulfide and hydrogen halide ^[6].



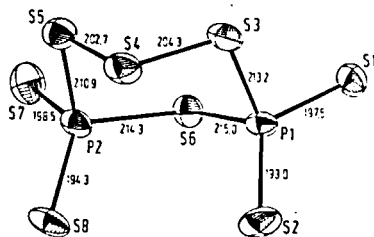
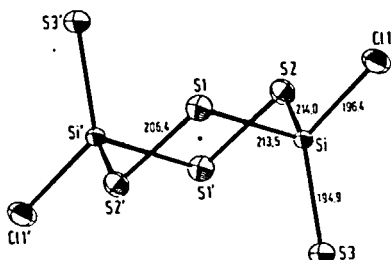
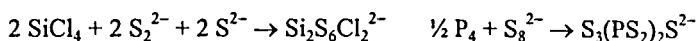
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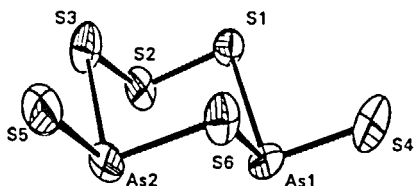
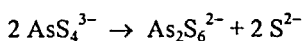
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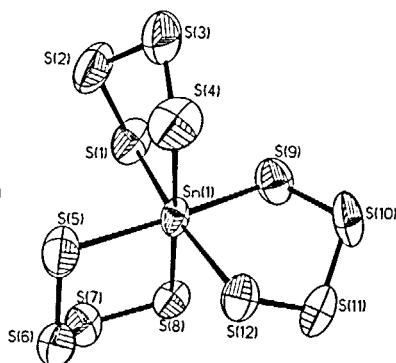
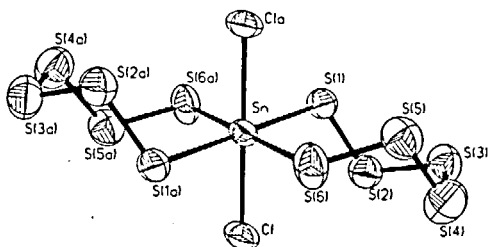
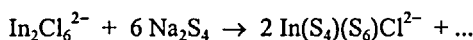
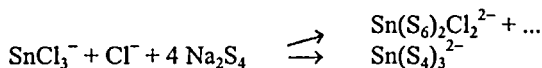
Reactions of SiCl_4 or P_4 with tetraphenylphosphoniumpolysulfide solutions produce compounds with ring structures in which more of the sulfur atoms are substituted ^[10]:

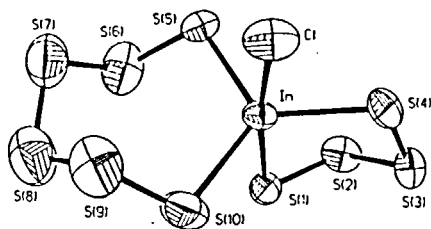


The surprising formation of another disubstituted sulfur ring resulted in the attempt to make $(\text{PPh}_4)_3\text{AsS}_4$ from Na_3AsS_4 and PPh_4Cl ; an intramolecular redox reaction was observed ^[11]:

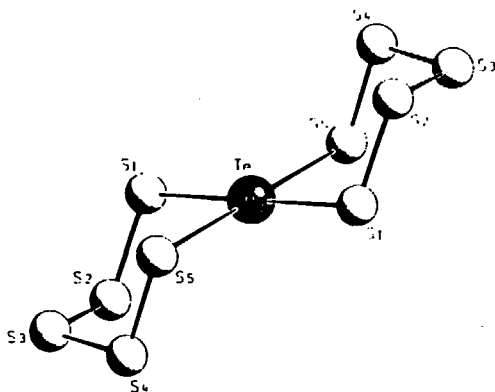
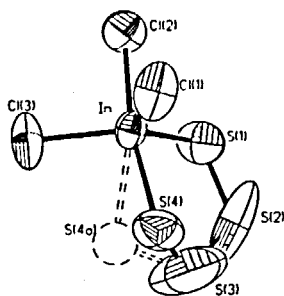
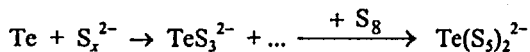
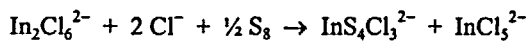


The simultaneous oxidizing and chelating potential of polysulfides can also be used in reactions with other elements that are not their highest oxidation state. Ring structures with the polysulfide ligands are the result, e.g. ^[7]:

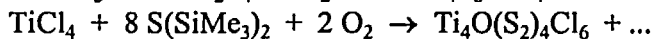
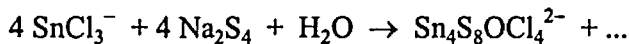


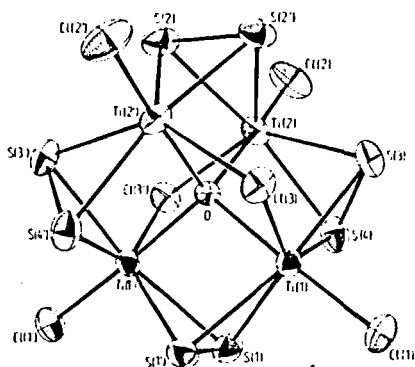
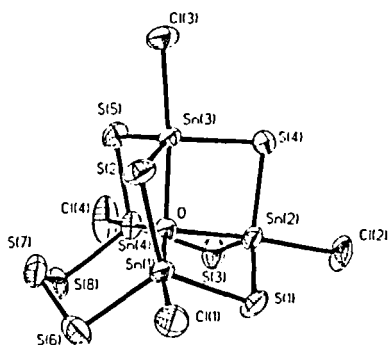


Similar compounds are also accessible by the action of elemental sulfur, e.g. ^[12,13]:

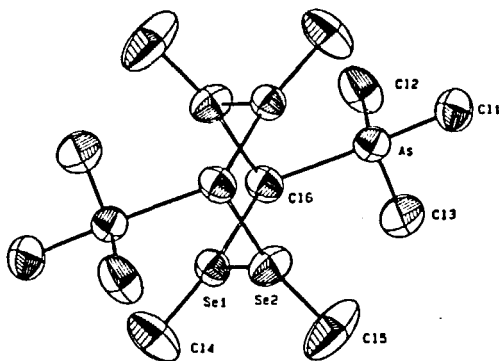
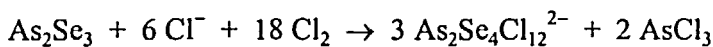


Partial hydrolysis ^[12] or the action of oxygen ^[14] during the reactions has resulted in cage structures having an oxygen atom in their centers:





Chloride and bromide ions are known to be able to act as bridging atoms between metal atoms. Nevertheless, the association of Se_2Cl_2 and AsCl_3 molecules via Cl^- ions was surprising^[15]:



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