Review

# Solvothermal Synthesis and Structure of Chalcogenidoarsenate Anions

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A rich variety of chalcogenidoarsenate anions and ligands have been prepared under mild solvothermal conditions in strongly polarizing solvents such as water, methanol and amines in the temperature range 100 – 200 °C. This review covers synthetic and structural aspects of such species $As_xE_y^{z-}$ with particular emphasis being placed on the trends and differences observed for $E$ = S, Se, Te and on developments within the past decade. These include the preparation of quaternary Main Group element chalcogenidoarsenates(III) such as $Cs_3AsGeSe_5$ and polymeric selenidoarsenates(II, III) such as $Cs_2As_4Se_6$. A currently expanding area of interest involves the employment of transition metal-polyamine or -polyimine fragments such as $\{Mn(tren)\}^{2+}$ or $\{Mn(terpy)\}^{2+}$ as structure-directing agents. The metal atoms of such cations can be connected to the terminal chalcogen atoms of oligomeric or polymeric anions $As_xE_y^{z-}$ to prevent their further condensation or can be directly incorporated into anionic or neutral networks when at least two free coordination sites are available in the fragment. This strategy has led to the characterization of novel ligands including *cyclo*-$[As_4S_8]^{4-}$, $As_2Se_6^{2-}$, $As_2Se_6^{4-}$ and $^1_\infty[As_4Se_7^{2-}]$. The syntheses and structures of the new compounds $Cs_5As_5Se_9$ and $Cs[\{Mn(trien)\}(AsSe_4\text{-}\kappa^2Se)]\cdot CH_3OH$ are also presented. Whereas the former phase contains infinite selenidoarsenate(II,III) chains $^1_\infty[As_5Se_9^{5-}]$, the $[\{Mn(trien)\}(AsSe_4)]^-$ anion of the latter compound represents the first example of a transition metal-containing ternary selenidoarsenate(V).

*Key words:* Arsenic, Sulfur, Selenium, Tellurium, Solvothermal Synthesis, Chalcogenidoarsenates