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 $\text{As}_x\text{E}_y^{2-}$ with particular emphasis being placed on the trends and differences observed for $\text{E} = \text{S}, \text{Se}, \text{Te}$ and on developments within the past decade. These include the preparation of quaternary Main Group element chalcogenidoarsenates(III) such as $\text{Cs}_3\text{AsGeSe}_5$ and polymeric selenidoarsenates(II, III) such as $\text{Cs}_2\text{As}_2\text{Se}_6$. A currently expanding area of interest involves the employment of transition metal-polyamine or -polyimine fragments such as $\{\text{Mn(tren)}\}^{2+}$ or $\{\text{Mn(terpy)}\}^{2+}$ as structure-directing agents. The metal atoms of such cations can be connected to the terminal chalcogen atoms of oligomeric or polymeric anions $\text{As}_x\text{E}_y^{2-}$ 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 $\text{cyclo-[As}_4\text{S}_8\]^{4-}$, $\text{As}_2\text{Se}_6^{2-}$, $\text{As}_2\text{Se}_6^{4-}$ and $\text{As}_2\text{Se}_7^{2-}$. The syntheses and structures of the new compounds $\text{Cs}_3\text{As}_4\text{Se}_9$ and $\text{Cs}[\{\text{Mn(trien)}\}^{+}\{\text{AsSe}_4\}^{\kappa_2\text{Se}}]\cdot\text{CH}_3\text{OH}$ are also presented. Whereas the former phase contains infinite selenidoarsenate(II,III) chains $\text{1}_\infty\{\text{As}_5\text{Se}_9\}^{5-}$, the $\{\{\text{Mn(trien)}\}^{+}\{\text{AsSe}_4\}\}^{2-}$ 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

Introduction

A rich variety of Group 13 – 15 chalcogenidometalates have been prepared both in molten alkali metal chalcogenide or polychalcogenide fluxes at 200 – 600 °C [1] and under mild solvothermal conditions in superheated polar fluids at 100 – 200 °C [2]. The solubility of inorganic starting materials such as metals, chalcogens and metal chalcogenides is greatly enhanced at elevated temperatures in such strongly polarizing media, and the prevailing reaction conditions in both techniques are suitable to support ion diffusion, but still mild enough to leave solution species such as chains and rings intact to participate in the construction of solid-state phases. A range of polar fluids such as $\text{H}_2\text{O}[2]$, $\text{CH}_3\text{OH}[3]$, $\text{NH}_3[2]$, $\text{en} (= \text{ethylenediamine})[4]$, $\text{dien} (= \text{diethylenetriamine})[5]$, $\text{tren} (= \text{tris(2-aminoethyl)amine})[6]$, and $\text{CH}_3\text{CN}[7]$ have been employed as reaction media for the solvothermal synthesis of chalcogenidoarsenates. However, the solubility of the inorganic components must often be enhanced by the addition of a mineralizer [8], which can be defined as a complexing agent capable of transporting ions from a starting material of low solubility to the site of product nucleation. The nuclearities and connectivity patterns of the chalcogenidoarsenate anions obtained under solvothermal conditions are influenced by the interplay of a wide range of parameters including the nature and molar ratio of the starting compounds, the viscosity of the reaction medium, temperature, reaction time, proton availability, oxidation potential of the solution, counter cation size, shape and charge, and product solubility [2].

Unlike its heavier homologs Sb and Bi, trivalent arsenic exhibits a remarkable reluctance to adopt hypervalent coordination polyhedra in its chalcogenido anions. To our knowledge, relatively undistorted $\psi$-$\text{AsE}_4$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) trigonal bipyramids have only been reported for the double chains $\text{1}_\infty\{\text{As}_6\text{S}_{10}^{2-}\}$ of $\{\text{Me}_4\text{N}\}_2\text{As}_6\text{S}_{10}[7]$. In this and other relevant coordination polyhedra (i. e. $\psi$-$\text{ME}_3$ tetrahedra and $\psi$-$\text{ME}_5$ octahedra) of trivalent Group 15 elements $\text{M}$, use of the Greek letter $\psi$ implies that one site is formally occupied by a non-bonded electron pair. The effective
trans-

### Table 1. Compounds containing discrete thio- or selenidoarsenate(III) anions with only $E^2$− ligands.

<table>
<thead>
<tr>
<th>Anion</th>
<th>$E = S$</th>
<th>$E = Se$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_3$E$_3$</td>
<td>As$_3$As$_3$S$_3$</td>
<td>As$_3$As$_3$Se$_3$</td>
</tr>
<tr>
<td></td>
<td>$A = Li$ [18], Na, K [19]</td>
<td>$A = Na, K$ [21]</td>
</tr>
<tr>
<td>cis-[As$_2$E$_4$]</td>
<td>[K(2,2,2-crypt)]$_2$</td>
<td>B$_2$As$_2$S$_2$ [20]</td>
</tr>
<tr>
<td></td>
<td>(As$<em>n$S$</em>{8-n}$)$_2$·2CH$_3$CN [23]</td>
<td>B$_2$As$_2$Se$_2$ [22]</td>
</tr>
<tr>
<td>trans-[As$_2$E$_4$]</td>
<td>B$_2$As$_2$S$_2$ [20]</td>
<td>B$_2$As$_2$Se$_2$ [22]</td>
</tr>
<tr>
<td>As$_2$E$_3$</td>
<td>[M(en)$_3$]$_2$As$_3$S$_3$</td>
<td>[M(en)$_3$]$_2$As$_3$Se$_3$</td>
</tr>
<tr>
<td>cyclo-[As$_4$E$_3$]</td>
<td>[enH$_2$]:[As$_4$S$_2$]·6en [26]</td>
<td>Cs$_4$As$_3$Se$_4$ [31]</td>
</tr>
<tr>
<td></td>
<td>[Fe(phen)$_3$]As$_3$S$_6$·dien·7H$_2$O [27], [Mn(dien)$_3$]$_2$[As$_4$Se$_5$]·30 refs. [13, 28]</td>
<td></td>
</tr>
<tr>
<td>cyclo-[As$_4$E$_3$]</td>
<td>Cs$_4$As$_3$Se$_4$ [31]</td>
<td></td>
</tr>
</tbody>
</table>

* Ref. [13]: [Mn(en)$_3$]$_2$[As$_4$Se$_4$]; ref. [28]: [NH$_4$(NH$_3$)$_4$][Ca(NH$_3$)$_2$]As$_3$S$_6$. 2NH$_3$ and [NH$_4$(NH$_3$)$_4$][Ba(NH$_3$)$_2$]As$_3$S$_6$·NH$_3$.

restriction to $\psi$-As$_3$E$_3$ ($E = S$, Se) tetrahedra as the basic building units for the construction of oligomeric and polymeric anions leads to a striking paucity in the number of structural types adopted by the thio- and selenidoarsenates(III) in comparison to the analogous chalcogenidoantimonates(III) [9]. However, in addition to chalcogenidoarsenates(III) containing As$E$−As bridges, a variety of compounds containing anions with trivalent arsenic atoms connected by oligochalcogenide ligands $E^2$− or directly bonded to one another have been isolated under solvothermal conditions. Most of these anions are without parallel for the chalcogenidoantimonates.

We have discussed the theory and practice of solvothermal techniques [2] for synthesizing chalcogenide-based materials of Main Group elements and have comprehensively reviewed the known chalcogenidoarsenates up to 1998 in previous articles [9, 10]. Although all types of chalcogenidoarsenate anions will be considered in the present review, its emphasis will, therefore, be placed on recent developments in the period 1998–2009. One currently expanding area of interest involves the employment of transition metal-polyamine or -polyimine fragments such as {Mn(dien)$_3$}$_2$+, {Mn(tren)$_2$}$_2$+ or {Mn(terpy)$_2$}$_2$+ (terpy = 2,2′:6′,2″-terpyridine) as structure-directing agents for the construction of novel ternary anions [4, 11]. The metal atoms of such cations can be connected with the terminal chalcogens of oligomeric or polymeric anions to prevent their further propagation or can be directly incorporated into anionic or neutral networks when two or more free coordination sites are available in the fragment. For instance, the 1D polymer $\frac{1}{m}$[Mn(tren)]([As$_3$Se$_7$] contains $\frac{1}{m}$[As$_4$Se$_5$]($E^2$−) double chains in which charge-compensating {Mn(tren)}$_2$+ fragments are coordinated by terminal Se atoms [12]. In contrast, the Mn atoms of {Mn(dien)}$_2$+ fragments participate in the $\frac{1}{m}$[MnAs$_3$S$_4$]− chains of [Mn(dien)$_3$]$_2$([Mn(dien)]$\mu$-As$_3$S$_4$)$_2$·4H$_2$O [13], in which the discrete [Mn(dien)$_2$]$^{2+}$ cations play a charge-balancing role. Other topics of recent interest have been the solvothermal synthesis of quaternary Main Group phases such as Cs$_5$As$_3$Ge$_3$Se$_9$ [14] and Cs$_4$Bi$_2$As$_3$Se$_7$ [15] and the isolation of novel binary lower oxidation state selenidoarsenates such as the $\frac{1}{m}$[As$_3$Se$_5$($E^2$−)] chain anions of Cs$_2$As$_2$Se$_6$ [16], which contain both As(II) and As(III) atoms.

In addition to reviewing the known chalcogenidoarsenate anions, we also report the synthesis and structure of two novel compounds, Cs$_4$As$_3$Se$_9$ and Cs$_3$[Mn(trien)](As$_3$S$_4$−$E^2$)·CH$_3$OH (trien = triethylenetetramine). Whereas the former phase contains a mixed oxidation state $\frac{1}{m}$[As$_3$Se$_5$($E^2$−)], the [{Mn(trien)]$\mu$Se$_4$}$^{−}$ anion of the latter compound represents to our knowledge the first example of a transition-metal-containing ternary selenidoarsenate(V).

### Chalcogenidoarsenates(III) Containing Only Chalcogenide Ligands $E^2$−

Trivalent arsenic sulfide As$_2$S$_3$ dissolves in aqueous alkaline solution to afford $\psi$-tetrahedral As$_3$S$_3$− anions together with oxo- and oxothio-anions. UV/Vis spectroscopic and potentiometric studies [17] have shown that mononuclear As$_3$S$_3$− anions readily condense to corner-bridged dipyrimal As$_2$S$_4$− and cyclic tripyramidal As$_3$S$_6$− anions, of which the latter species predominate at pH ≤ 11. Both As$_2$E$_5$− [24, 25] and cyclo-As$_3$E$_3$− [13, 26–30] have been isolated for $E = S$, Se in the presence of suitable cations (Table 1) from chalcogenidoarsenate(III) reaction solutions in heated ethylenediamine or diethylenetriamine, e. g. in the case of [Fe(phen)$_3$]As$_3$S$_6$·dien·7H$_2$O [27] from a dien/water mixture containing FeCl$_3$, phen,
Solvothermal Synthesis and Structure of Chalcogenidoarsenate Anions

Fig. 1. The cyclo-[As₃Se₆]³⁻ and cyclo-[As₄Se₈]⁴⁻ anions of (a) [Sr(en)₄]₂(As₃Se₆)Cl [29] and (b) Cs₄As₄Se₈ [31]. In this and Figs. 5 – 19, shaded circles represent As atoms, cross-hatched circles metal atoms, and open large circles S and Se atoms.

As₅O₃ and S (molar ratio 1 : 3 : 2 : 6) at 140 °C. An analogous solvothermal strategy was employed for the preparation of the complexes [M(en)₃]₂As₂E₅ (E = S, M = Mn, Ni; E = Se, M = Mn, Co) [24, 25] and [Mn(dien)₂]₃(As₃Se₆)₂ [30], which were synthesized from As₂O₃ and the appropriate chalcogen E and metal chloride MCl₂ in respectively en and dien reaction solutions at T = 140 °C. In contrast, the cyclic As₃E₆³⁻ anions of [enH₂]₃(As₃S₆)₂·6en [26] and [Sr(en)₄]₂(As₃Se₆)Cl [29] (Fig. 1a) were obtained directly by dissolving respectively As₂S₃ or As₂Se₃ in refluxing ethylenediamine, in the latter case in the presence of SrCl₂ to afford the suitable complex cation [Sr(en)₄]²⁺. The more polar terminal As–Et bonds in these As₃E₆³⁻ and other chalcogenidoarsenate anions are significantly shorter than the accompanying bridging As–Eb bonds. The differences are exemplified by the As–Sₜ and As–Sₜ distances of 2.153 – 2.159 and 2.274 – 2.314 ˚Å, respectively, in [enH₂]₃(As₃S₆)₂ and the As–Seₜ and As–Seₚ bond lengths of 2.288–2.296 ˚Å and 2.398–2.424 ˚Å in [Sr(en)₄]₂(As₃Se₆)Cl. Interestingly, the cage-like As(II) sulfide, realgar As₄S₄, was employed as the source for both the edge-bridged cis-[As₂S₄]²⁻ anions in [K(2.2.2-crypt)]₂As₂S₄·2CH₃CN [23] and the corner-bridged As₃S₄³⁻ anions of [NH₄(NH₃)₄]Ca(NH₃)₃As₃S₄·2NH₃ and [NH₄(NH₃)₄][Ba(NH₃)₇]-As₃S₄·NH₃ [28], all of which were prepared by oxidation of the respective alkali or alkaline earth metals (K or Ca/Ba) in liquid ammonia. These differing synthesis protocols emphasize the importance of structure-directing counter cations for the isolation of a particular chalcogenidoarsenate and also point to the possible role of redox equilibria in determining the nature of the anionic species, a topic that will be highlighted in the following sections. A case in point is provided by the cyclo-[As₄Se₈]⁴⁻ anion (Fig. 1b) of Cs₄As₄Se₈ [31], which was obtained as a by-product of the disproportionation reaction of the ¹[AsSe(µ-Se₂)]⁻ chains of CsAsSe₃·0.5H₂O to the mixed oxidation state selenidoarsenat(II,III) Cs₂As₃Se₆ [16] and the polyselenide Cs₂Se₅ in superheated methanol at 190 °C. It is interesting to note that no telluridoarsenate anions with As–Te–As linkages appear to be known.

Discrete pyramidal AsE₃³⁻ (E = S, Se) anions have been structurally characterized in the phases Li₃AsSe₃ [18], A₃AsE₃ (A = Na, K) [19, 21] and Ba₂As₂E₅ [20, 22], all of which were first prepared in high temperature fluxes, e. g. in the case of Na₃AsS₃ by tempering a mixture of Na₂S, As and S in a sealed glass tube at 420 °C for 10 d [19b]. However, the potassium compounds K₃AsE₃ (E = S, Se) have also been obtained as brown powders on evaporation of ammonia solutions containing stoichiometric quantities of K, As₂E₅ and E [32].

The reluctance of trivalent arsenic to extend its effective coordination sphere beyond pyramidal severely limits the number of potential structure types available for polymeric chalcogenidoarsenate(III) anions. Condensation of the predominant solution species AsS₃³⁻, As₂S₅⁴⁻ or cyclo-[As₃S₆]³⁻ under mild solvother-
nical conditions might be expected to generate a family of structurally related polymeric chain anions \( \frac{1}{n}[^{2}\text{As}_{2}^3\text{S}_{3+n+1}^2]^{-} \) \((x = 1 - 4)\), whose connectivity patterns are illustrated in Fig. 2. As listed in Table 2, 1D thioarsenates(III) of the formula types \( A_{2}[\text{As}_{2}^3\text{S}_{3x+1}] \) have indeed been isolated for \( x = 1 - 4 \) by employing either alkali metal or alkylammonium cations as structure-directing agents. However, whereas the postulated structure types \( a, b \) and \( d \) of Fig. 2 have been confirmed in the phases \( \text{AAsS}_{2} \) (type \( a, A = \text{Na, Rb} [33, 34], \) \( \text{A}_{2}\text{As}_{2}^3\text{S}_{7} \) (type \( b, A = \text{Me}_{4}\text{N} [7] ), \( \text{A}_{2}\text{As}_{2}^4\text{S}_{13} \) (type \( d, A = \text{Et}_{4}\text{N} [35]), \) and \( \text{A}_{2}\text{As}_{8}^6\text{S}_{13} \cdot \text{H}_{2}\text{O} \) (type \( d, A = \text{K, Rb, NH}_{4} [36], \) modified connectivity patterns (Fig. 3) were established for the \( \frac{1}{n}[\text{As}_{6}^3\text{S}_{10}^{2-}]^{-} \) anions of \( (\text{Me}_{2}\text{N})_{2}\text{As}_{8}^6\text{S}_{10} [7] \) and \( (\text{Et}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{10} [35]. \) The \( \text{zweier} \) repeating units depicted for the metathioarsenate(III) chains \( \frac{1}{n}[\text{As}_{2}^3\text{S}_{4}^{2-}]^{-} \) of type \( a \) in Fig. 2 are observed in \( \text{NaAsS}_{2} \), but \( \text{vierer} \) chains are present in \( \text{RbAsS}_{2} \). In contrast to \( \text{NaAsS}_{2} \), which was prepared by heating \( \text{As}_{2}^3\text{S}_{3} \) in an \( \text{Na}_{2}\text{S} \) flux at 220 °C, \( \text{RbAsS}_{2} \) was isolated together with the phase \( 3\text{Rb}_{2}\text{As}_{8}^6\text{S}_{6} \cdot \text{As}_{3}^3\text{S}_{3} \) by methanolothermal reaction of \( \text{Rb}_{2}\text{CO}_{3} \) with \( \text{As}_{2}^3\text{S}_{3} \) (type \( d \) for \( T = 200 \) °C, \( 7 \) d) led to the formation of the more highly condensed \( \frac{1}{n}[\text{As}_{6}^3\text{S}_{10}^{2-}]^{-} \) chains of \( \text{Rb}_{2}\text{As}_{8}^6\text{S}_{13} \cdot \text{H}_{2}\text{O}. \) The isostructural phases \( \text{A}_{2}\text{As}_{2}^4\text{S}_{13} \cdot \text{H}_{2}\text{O} \) with \( A = \text{K, NH}_{4} \) were obtained in a similar manner [36]. The alkali metal carbonates \( \text{A}_{2}\text{CO}_{3} \) (\( A = \text{K, Cs} \) used in these syntheses have been found to be particularly useful for the solubilization of arsenic and other Group 14/15 element chalcogenides under mild hydrothermal or methanolothermal conditions [2]. It can be assumed that reaction equilibria such as (1) are involved that are driven to the right by the release of \( \text{CO}_{2}. \)

\[
3\text{CO}_{2}^{2-} + \text{As}_{2}^3\text{S}_{3} = \text{AsE}_{3}^{3-} + \text{AsO}_{3}^{2-} + 3\text{CO}_{2} \tag{1}
\]

The contrasting products for the hydrothermal and methanolothermal reactions of \( \text{Rb}_{2}\text{CO}_{3} \) with \( \text{As}_{2}^3\text{S}_{3} \) highlight two general aspects of the solvothermal synthesis of thioarsenate anions. Firstly, the greater tendency of water to self-ionize \( [p\text{K}_{\text{auto}}(\text{CH}_{3}\text{OH})–p\text{K}_{\text{auto}}(\text{H}_{2}\text{O}) = 3.2] [38] \) favors the formation of highly condensed polyanions as in reaction (2) by providing more protons to remove the resulting \( \text{S}^{2-} \) anions as \( \text{HS}^{-}. \)

\[
2\text{As}_{3}^3\text{S}_{6}^{3-} + \text{As}_{2}^3\text{S}_{5}^{4-} = \frac{1}{n}
[\text{As}_{6}^3\text{S}_{13}^{2-}]_{n} + 4\text{S}^{2-} \tag{2}
\]

Secondly, employment of alkali metal carbonates can also lead to the concomitant formation of reduction products such as the \( \text{As}_{4}^4\text{S}_{6}^{2-} \) anions and the dimorphic \( \text{As}_{5}^3\text{S}_{5} \) molecules of \( \text{Rb}_{2}\text{As}_{4}^3\text{S}_{6} \cdot \text{As}_{3}^3\text{S}_{7} \). A thermodynamically plausible stoichiometric reaction (3) can be formulated for the methanolothermal reaction of \( \text{Rb}_{2}\text{CO}_{3} \) and \( \text{As}_{2}^3\text{S}_{3} \) as follows:

\[
24\text{Rb}_{2}\text{CO}_{3} + 35\text{As}_{2}^3\text{S}_{3} \\
= 3 [3 \text{Rb}_{2}\text{As}_{4}^3\text{S}_{6} \cdot \text{As}_{3}^3\text{S}_{7} + 18 \text{RbAsS}_{2} \tag{3}
+ 4 \text{Rb}_{2}\text{AsO}_{3} + 24\text{CO}_{2} + 6\text{SO}_{2}
\]

Whereas the alkylammonium thioarsenates(III) \( (\text{Me}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{10} \) and \( (\text{R}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{10} \) \((R = \text{Me, Et})\) may be prepared under very mild solvothermal conditions by treatment of \( \text{As}_{2}^3\text{S}_{3} \) with \( \text{Na}_{2}\text{S} \) in the presence of \( (\text{R}_{4}\text{N})\text{Cl} \) in acetonitrile at 110 °C [7, 35], much more forcing hydrothermal conditions \((T = 180 \) °C) are required to obtain the highly condensed phase \( (\text{Et}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{13} \) from such starting materials. Alternating corner bridging of \( \text{cyclo}[^{2}\text{As}_{8}^6\text{S}_{8}]^{2-} \) and pyramidal \( \text{As}_{3}^3\text{S}_{3}^{2-} \) anions generates the \( \frac{1}{n}[\text{As}_{6}^3\text{S}_{10}^{2-}]^{-} \) chains (Fig. 2, type \( b \) of \( (\text{Me}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{7} \). Although the direct linkage of \( \text{cyclo}[^{2}\text{As}_{8}^6\text{S}_{8}]^{2-} \) anions (Fig. 2, type \( c \) is clearly recognizable in the \( \frac{1}{n}[\text{As}_{6}^3\text{S}_{10}^{2-}]^{-} \) anions of \( (\text{Me}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{10} \) (Fig. 3a), these individual chains are joined together into double chains through planar \( \text{As}_{2}^3\text{S}_{2} \) rings, whose arsenic atoms exhibit relatively undistorted \( \psi \)-trigonal bipyramidal coordination geometries. Contrasting bond lengths of 2.533(3) and 2.202(2) Å are observed for the respectively axial and equatorial \( \text{As–S} \) bonds within the four-membered rings. In contrast, one half of the potential \( \text{As}_{3}^3\text{S}_{7} \) rings in the related \( \frac{1}{n}[\text{As}_{6}^3\text{S}_{10}^{2-}]^{-} \) double chains of \( (\text{Et}_{4}\text{N})_{2}\text{As}_{8}^6\text{S}_{10} \) (Fig. 3b) appear to have opened to afford linear bridging units \( \text{As}_{2}^3\text{S}_{7}^{5-} \cdot \text{R}_{2}\text{As} \) and the condensation grade \( c \) \((c = 2x/(3x + 1)) \) of the resulting polyanion \((e.g. c = 0.50 \text{ for Na}^{+}, \ c =

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>( 2x )</th>
<th>Condensation grade</th>
<th>Ca</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.50</td>
<td>( \text{NaRb} )</td>
<td>33, 34</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.571</td>
<td>( \text{Me}_{2}\text{N} )</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>( \text{Me}<em>{4}\text{N}, \text{Et}</em>{4}\text{N} )</td>
<td>7, 35</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.615</td>
<td>( \text{A}(\text{H}<em>{2}\text{O}), A = \text{K, Rb, NH}</em>{4} )</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

\( c = 2x/(3x + 1). \)
0.615 for Cs⁺) is clearly apparent for the alkali metal thioarsenates(III) listed in Table 2. This trend is due to the fact that the number of potentially available chalcogen coordination partners per unit of anion charge increases with the value of parameter c [10].

In contrast to the general size-related structure-directing role of the counterions in the 1D thioarsenates(III), a specific templating role is adopted by the Cs⁺ cations in the only known lamellar phase, Cs₂As₈S₁₃ [37]. As illustrated in Fig. 4, the alkali metal cations induce the formation of eight-membered As₄S₄ rings and are coordinated by each of the four S atoms of the individual rings in the resulting crystal structure. It is interesting to note in this respect that discrete cyclo-[As₄E₈]⁴⁻ anions have only been observed in Cs₄As₄Se₈ [31], once again in the presence of Cs⁺ counter cations. An interesting feature in both Cs₂As₈S₁₃ and the 1D thioarsenates(III) is the adoption of the unusual axial site relative to the cyclic building units by the free terminal S atoms, which allows these to participate in weak S⋯As secondary bonding (e.g. S⋯As distances of 3.053(3) and 3.118(3) Å in (Me₄N)₂As₂S₇) to the other ring As atoms.

In striking contrast to the thioarsenate(III) system, hydrothermal reaction of alkali metal carbonates A₂CO₃ (A = K, Rb, Cs) with As₂Se₃ affords the compounds KAsSe₂·H₂O and AAsSe₂·0.5H₂O (A = Rb, Cs), in which ψ-As₆Se₈ tetrahedra are linked through Se–Se bonds into ₂[As₆Se₈]⁻ chains [39]. This connectivity pattern is without parallel for the thioarsenates(III) and will be discussed in more detail below. Attempts to prepare alkylammonium selenidoarsenates(III) in acetonitrile were also unsuccessful, e.g. treatment of (Et₄N)Cl with As₂Se₃ and Na₂Se in acetonitrile at 110 °C (t = 11 d) affords (Et₄N)[SeAs(Se₇-k²Se₁,Se₇)] in good yield [35]. Somewhat surprisingly, the metaselenidoarsenates(III) AAsSe₂ (A = K–Cs) with their ₂[As₆Se₈⁻] chains can, however, can be prepared from A₂CO₃ and As₂Se₃ under mild methanolothermal conditions [40]. Together with the analogous lithium and sodium salts they have also been obtained by a high-temperature flux reaction of the same components at 650 °C [41a] or, in the case of NaAsSe₂, by direct reaction of the elements at 700 °C [41b]. Whereas zweier repeat units are observed for NaAsSe₂ and CsAsSe₂, longer vierer units are found in both KAsSe₂ and RbAsSe₂ [40]. The failure of As₆Se₈³⁻ anions to self-condense to polyseleidoarsenates(III) with a condensation grade c > 0.5 under solvothermal conditions may be due to (a) the decrease in As–E bond strength on going from E = S to Se and (b) the significantly higher acidity of HSe⁻ in comparison to HS⁻. As a result of factor (b), removal of E²⁻ anions resulting from self-condensation reactions such as (2) will be less favorable for E = Se in comparison to E = S.

The characteristic tendency of pyramidal As₅S₃³⁻ anions to first condense through corner-bridging to As₅S₆⁴⁻ and cyclo-[As₅S₆]³⁻ anions and subsequently to 1D polymeric thioarsenate(III) anions under mild hydrothermal conditions in the presence of suitable counterions has already been discussed. This abil-
ity to self-condense to afford tailored building units of suitable size, hapticity and charge has also proved to be particularly useful for the synthesis of ternary and quaternary thioarsenate(III) anions containing a wide range of metal ions. The following types of thioarsenate(III) ligands have been reported:

(1) $\text{AsS}_3^{3–}$ in $\alpha$- and $\beta$-$\text{Ag}_3\text{AsS}_3$ [42], $\text{TL}_2\text{SnAs}_2\text{S}_6$ [43], $\text{KCu}_2\text{AsS}_3$, $\text{KCu}_4\text{AsS}_3$ [44], $\text{K}_2[\text{Ag}_6(\text{AsS}_3)\langle\text{As}_3\text{S}_7\rangle]$ [32], $\text{K}_2\text{SnAs}_2\text{S}_6$ [45], $\text{THgAsS}_3$ [46], $\frac{1}{2}[\{\mu\text{phen}\}\{\text{In}(\text{Ph}_4\text{P})\}_2]\text{InAsS}_4$ [47] and $\frac{3}{2}[\{\text{In}(\text{Ph}_4\text{P})\}_2\{\text{In}(\text{NO}_3)\}_3,\text{As}_2\text{S}_3$ and $\text{S}$ at $T = 300$ $\circ$C [44]. Particularly interesting aspect of the $\frac{2}{3}[\text{Cu}_2\text{AsS}_3^{3–}]$ sheets of $\text{KCu}_2\text{AsS}_3$ is the tetrahedral coordination of half of their copper atoms by three sulfur atoms from different $\text{AsS}_3^{3–}$ building units together with the arsenic lone pair of a fourth such pyramidal anion. The polyamine tren was employed both as a tetradentate coligand for the charge-balancing $\text{Mn}(II)$ atoms and as the solvothermal reaction medium for the generation of $\frac{1}{3}[\{\mu\text{tren}\}\{\text{InAsS}_4\}]$ [47] from $\text{MnCl}_2$, $\text{In}(\text{NO}_3)_3$, $\text{As}_2\text{S}_3$ and $\text{S}$ at $T = 160$ $\circ$C. Pyramidal $\text{AsS}_3^{3–}$ units share corners with dinuclear $\text{In}_2\text{S}_6^{6–}$ units to construct 1D chains (Fig. 5), whose charge is balanced by peripheral $[\{\mu\text{tren}\}\text{Mn}]^{2+}$ fragments.

Both $\text{AsS}_3^{3–}$ pyramids and linear $\text{As}_8\text{S}_7^{5–}$ chains participate in the $\frac{1}{3}[\text{Ag}_3\text{AsS}_2\text{S}_5]$ layers of $\text{KAg}_3\text{AsS}_5$, which was obtained by treating $\text{K}_2\text{AsS}_3$ with $\text{AgBF}_4$ at a 1:3 molar ratio in superheated methanol at $T = 110$ $\circ$C [32]. Kanatzidis et al. have employed

Fig. 5. A segment of the infinite chain structure of the quaternary thioarsenate(III) $\frac{1}{3}[\{\text{Mn}(\text{tren})\}\text{InAsS}_4]$ [47].
a general hydrothermal strategy involving treatment of a precursor AAsS$_3$ (A = K, Rb) with the appropriate metal chloride (BiCl$_3$, HgCl$_2$, PdCl$_2$, InCl$_3$, NiCl$_2$) or oxide (MoO$_3$) in the presence of (Me$_4$N)Cl or (Ph$_4$P)Br in superheated water to afford the listed ternary tetramethylammonium and tetraphenylphosphonium thioarsenate(III) [52–54, 57]. The suitability of the protic aqueous medium for inducing self-condensation of As$_3$S$_3$$^{3−}$ anions is underlined by the wide variety of linear and cyclic building units found in these compounds. Only the formally negative terminal S atoms participate in metal atom coordination in the reported ternary tetramethylammonium and tetraphenylphosphonium thioarsenate(III), but it is worth noting that Mn–S bonds to bridging S atoms are present in the infinite sheets of [Mn$_2$(2,2′-bpy)As$_2$S$_5$] (2,2′-bpy = 2,2′-bipyridyl) [5]. A structure-directing influence of the incorporated metal atoms on both the nuclearity and connectivity pattern of the building units is often apparent in ternary thioarsenate(III) anions. For instance, the construction of the lamellar cycles units is often apparent in ternary thioarsenate(III) anions, and this is also the case for the polymeric anionic (Me$_4$N)$_2$Rb[As$_4$S$_7$] [54] facilitated by the presence of a smaller Rb$^+$ cation (from the starting material) in addition to two Me$_4$N$^+$ cations. The tridentate chair-shaped cyclo-[As$_3$S$_6$]$^{3−}$ ligands exhibit crystallographic C$_3$ symmetry and coordinate the Bi(III) atoms in an octahedral manner through their terminal S atoms. An analogous connectivity pattern can be recognized for the thioarsenate(III) ligands and the hexacoordinated Sn(IV) atoms of the likewise trigonal phase K$_2$SnAs$_2$S$_6$ [45], whose denser $\frac{1}{2}$[Sn(As$_3$)$_2$]$^{2−}$ sheets contain simple tridentate As$_3$S$_3$$^{3−}$ pyramids rather than condensed trinuclear cyclo-[As$_3$S$_6$]$^{3−}$ ligands.

Dinuclear corner-bridged As$_2$S$_5$$^{4−}$ units have been found in a wide range of compounds including the minerals Tl$_2$MnAs$_2$S$_5$ [49], TiCuPbAs$_2$S$_5$ [50] and TlAgPbAs$_2$S$_5$ [51]. The linear As$_3$S$_7$$^{3−}$, As$_4$S$_9$$^{5−}$ and As$_5$S$_{11}$$^{7−}$ ligands of (Ph$_4$P)$_2$[InAs$_3$S$_7$] [54], K$_2$[Ag$_6$(As$_3$S$_7$)] [32], (Ph$_3$P)$_2$[Hg$_2$As$_4$S$_9$] [57] and the mineral [Cu$_{12}$(As$_3$S$_7$)(As$_5$S$_{11}$)] [59] are known as binary thioarsenate(III) anions, and this is also the case for the polymeric $\frac{1}{2}$[As$_3$S$_6$$^{3−}$], $\frac{1}{2}$[As$_4$S$_7$$^{2−}$] and cyclo-[As$_4$S$_8$$^{4−}$] anions of (Me$_4$N)[Hg$_2$As$_4$(As$_2$S$_2$)] [57], $\frac{1}{2}$[Mn(tren)]As$_4$S$_7$ [48] and $\frac{1}{2}$[Mn(terpy)]$_2$(μ-As$_4$S$_8$) [48], respectively. The infinite $\frac{1}{2}$[As$_3$S$_6$$^{3−}$] anions contain As$_2$S$_4$ repeating units in which one of the arsenic atoms shares its terminal S atom with an additional pyramidal As$_5$S$_{11}$$^{7−}$ unit. In contrast to the polymeric thioarsenate(III) anions of the same formula type in (Me$_4$N)$_2$As$_4$S$_7$ [7], the $\frac{1}{2}$[As$_4$S$_7$$^{2−}$] anion of $\frac{1}{2}$[Mn(tren)]As$_4$S$_7$ contains cyclo-[As$_4$S$_8$$^{4−}$] rather than cyclo-[As$_5$S$_{11}$$^{7−}$] building blocks. Connection of these eight-membered rings through corner-bridged dinuclear As$_2$S$_5$$^{4−}$ units leads to the generation of the infinite double chains depicted in Fig. 6. Further condensation is prevented by the charge-balancing {Mn(tren)}$^{2+}$ fragments that are attached to half of the terminal S atoms. $\frac{1}{2}$[Mn(tren)]As$_4$S$_7$ was prepared by hydrothermal reaction of [MnCl$_2$(tren)] with As$_2$S$_3$ at a 1:1 molar ratio at 160 °C in the presence of an equivalent of the mineralizer Cs$_2$CO$_3$ [48].

The meridional coordination mode of the tridentate terpy ligand enables the pentacoordinated Mn(II) atoms of the {Mn(terpy)}$^{2+}$ fragment to adopt a wide range of E–Mn–E′ angles (96–121°) in its chalcogenidoarsenate(III) complexes. Treatment of [{Mn(terpy)}] with As$_2$S$_3$ and Cs$_2$CO$_3$ at an equimolar ratio in a superheated 10:1 H$_2$O/en mixture leads to the formation of [{Mn(terpy)}$_2$(As$_4$S$_8$)] (Fig. 7) at 150 °C and to the coordination polymer $\frac{1}{2}$[{Mn(terpy)}(As$_2$S$_3$)] (Fig. 8) at 190 °C [48]. The cyclo-[As$_4$S$_8$$^{3−}$] ligands of the former compound are unknown as isolated anions and chelate the Mn(II) atoms through adjacent terminal S atoms to generate relatively narrow S–Mn–S′ angles of 101.3(1)°. Such dinuclear units are linked through weak Mn···S interactions of length 2.843(4) Å into infinite chains.
It is interesting to note in this respect that the isomeric As$_4$S$_8^{4-}$ ligands of (Ph$_4$P)$_2$[Ni(μ-As$_4$S$_6$)] [52] contain a central corner-bridged cyclo-[As$_2$S$_4^{2-}$] unit to which corner-sharing pyramidal As$_3S_3^{3-}$ units are attached in a trans arrangement. These As$_4$S$_8^{4-}$ ligands chelate Ni(II) atoms in the square-planar configuration and bridge to the next metal atom in an infinite $\{\text{Ni}(\mu-\text{As}_4\text{S}_6)^2\}$ chain. A central corner-bridged cyclo-[As$_2$S$_4^{2-}$] unit is also present in the longer As$_6S_{12}^{6-}$ units of the mineral Tl$_2$[Pb$_2$(As$_6$S$_{12}$)] [60], but in this case the attached dinuclear As$_2$S$_5^{4-}$ units are sited cis to one another. The structure of the higher temperature phase $\frac{1}{\omega}$[[Mn(terpy)](As$_2$S$_4$)] is illustrated in Fig. 8. It can be regarded as containing $\frac{1}{\omega}$[[As$_2S_2^{2-}$] chains that coordinate Mn(II) atoms through their terminal S atoms and incorporate these into ten-membered Mn$_2$S$_3$ rings that are fused at As–S–As linkages. The Mn(II) atoms display a distorted trigonal bipyramidal environment with equatorial N–Mn–S angles of 120.8(2) and 123.2(2)$^\circ$ to the central imino nitrogen atom complementing the relatively wide S–Mn–S$'$ angle of 115.6(1)$^\circ$ within the $\frac{1}{\omega}$[[MnAs$_2$S$_4$] double chain.

An unprecedented gondola-like structure has been established for the [Pd$_7$As$_{10}$S$_{22}$]$^{4-}$ anion of (Ph$_4$P)$_4$[Pd$_7$As$_{10}$S$_{22}$], which was prepared by methanolothermal reaction of PdCl$_2$ with K$_3$AsS$_3$ and (Ph$_4$P)Br at 110 $^\circ$C for 3 days [53]. As may be seen in Fig. 9, two different thioarsenate ligands, As$_2$S$_5^{4-}$ and As$_3$S$_6^{5-}$, are linked to Pd(II) atoms in the square-planar configuration in this remarkable anion. The As$_3$S$_6^{5-}$ units bind to two palladium atoms and can be regarded as being a two electron reduction product of the linear As$_3S_7^{5-}$ unit:

$$\text{As}_3S_7^{5-} + 2e^- \rightarrow \text{As}_3S_6^{5-} + S^{2-}$$

As$_3S_3^{3-}$ anions could provide the reducing agent for reaction (4) and would be oxidized to AsS$_4^{3-}$ anions in the process [53]. A similar two electron reduction involving cyclic As$_3S_6^{3-}$ anions has been reported for the analogous hydrothermal reaction of PtCl$_2$, K$_3$AsS$_3$ and (Ph$_4$P)Br at 110 $^\circ$C [58]. Oxidation of Pt(II) atoms to Pt(IV) provides the electrons for the reduction in this case. Each of the resulting cyclo-[As$_3S_3^{3-}$] anions in the product (Ph$_4$P)$_2$[Pt(As$_3$S$_5$)$_2$] coordinates the central Pt(IV) atom in a tridentate manner through its remaining two terminal S atoms and the negatively charged arsenic atom.

The following types of selenidoarsenate(III) ligands have been characterized in ternary anions:

1. $\frac{1}{\omega}$[[As$_3$Se$_2^{2-}$]
   - in K$_2$AgAs$_2$Se$_6$, Rb$_2$AgAs$_3$Se$_6$ [61],
   - CsAgAs$_2$Se$_4$, Cs$_3$AgAs$_4$Se$_8$ [62].

2. As$_3$Se$_3^{3-}$
   - in $\alpha$- and $\beta$-Ag$_3$AsSe$_3$ [63, 32],
   - Cs$_3$As$_2$Se$_5$ [64],
   - A$_3$[M$_2$Se$_2$(Se$_2$)$_3$(AsSe$_3$)$_2$]$_2$ (A = K, Rb, Cs; M = Nb, Ta) [65].

3. As$_2$Se$_5^{4-}$
   - in K$_3$AgAs$_2$Se$_5$·0.25 CH$_3$OH [61],
   - (Me$_3$N)$_2$[Ag$_3$As$_2$Se$_5$] [32],
   - (Et$_3$N)$_2$[M$_2$O$_2$Se$_2$(μ-As$_2$Se$_3$)] [52].

4. cyclo-[As$_3$Se$_6^{3-}$] – in RbAg$_2$As$_3$Se$_6$ [66]

5. $\frac{1}{\omega}$[[As$_4$Se$_2^{2-}$]
   - in $\frac{1}{\omega}$[[Mn(tren)]As$_2$Se$_4$] [12].

6. cyclo-[As$_4$Se$_8^{4-}$]
   - in $\frac{1}{\omega}$[[Mn(terpy)]$_2$(μ-cyclo-(As$_4$Se$_8$))] [48].

With the exception of $\alpha$-Ag$_3$AsSe$_3$, which was synthesized from a high-temperature flux of the elements.

Fig. 8. A segment of the infinite chains of $\frac{1}{\omega}$[[Mn(terpy)](As$_2$S$_4$)] [48].

Fig. 9. The gondola-like structure of the [Pd$_3$(As$_3$S$_6$)$_2$-Pd(As$_3$S$_5$)$_2$]$^{4-}$ anion of (Ph$_4$P)$_4$[Pd$_7$As$_{10}$S$_{22}$] [53] with its As$_3$S$_6^{5-}$ and As$_5S_7^{5-}$ ligands.
at 1000 °C for 4 d [63], all of these compounds have been isolated under mild solvothermal conditions in either superheated water or methanol. For instance the silver-containing quaternary phases K₂Ag₃As₅Se₆, Rb₂Ag₃As₅Se₆, K₃Ag₂As₅Se₅·0.25 CH₃OH [61], Cs₃Ag₄As₄Se₈, and CsAgAg₂Se₄ were all prepared by methanolothermal reaction of AsSe₃⁻ anions (sources Li₃AsSe₃ or K₃AsSe₃) with AgBF₄ in the presence of the appropriate alkali metal cation at temperatures in the range 120–140 °C. Methanolothermal conditions (elemental As, Ge and Se at 190 °C in the presence of Cs₂CO₃) were also employed to synthesize Cs₃AsGeSe₅, which represents the first example of a mixed Ge(IV)/As(III) chalcogenidometalate and contains both the linear As₂Se₅⁻ anion and the ring-shaped anions cyclo-[As₂Se₄]⁻, x = 3, 4. Although infinite As₄Se₇⁻ chains have been found in five different compounds, no examples for linear ligands [AsₙSeₙ₊₁]⁺⁻ (x = 3–5) appear to be known. Several of the compounds have thioarsenate(III) analogs, for instance (Et₄N)₂[(Mo₂O₂Se₂)(µ-As₂Se₃)] [52], [₁⁺[(Mn(tren)]ASSe₇] [12] and [(Mn(terpy)]₂AS₄Se₈] [48]. In the molybdenum(V) complexes, [Mo₂O₂E₂]²⁺ cores (E = S, Se) are linked by corner-bridged dinuclear As₂E₄⁻⁻ ligands which chelate neighboring metal atoms through their terminal chalcogen atoms.

The manganese(II) complexes ₁⁺[(Mn(tren)]AS₃Se₇] and [(Mn(terpy)]₂AS₄Se₈] were obtained under hydrothermal conditions at 150 °C by treating MoO₃ with K₃AsSe₃ and (Et₄N)Br at a 1:4:6 molar ratio at 110 °C for 7 d [52].

The list of ternary selenidoarsenate(III) ligands contains both the linear As₂Se₅⁻⁺ anion and the ring-shaped anions cyclo-[As₂Se₄]⁻⁻, x = 3, 4. Although infinite [AsₙSeₙ₊₁]⁺⁻ (x = 3–5) appear to be known. Several of the compounds have thioarsenate(III) analogs, for instance (Et₄N)₂[(Mo₂O₂Se₂)(µ-As₂Se₃)] [52], ¹⁺[(Mn(tren)]AS₄Se₇] [12] and [(Mn(terpy)]₂AS₄Se₈] [48]. In the molybdenum(V) complexes, [Mo₂O₂E₂]²⁺ cores (E = S, Se) are linked by corner-bridged dinuclear As₂E₄⁻⁻ ligands which chelate neighboring metal atoms through their terminal chalcogen atoms. The manganese(II) complexes ¹⁺[(Mn(tren)]AS₃Se₇] and [(Mn(terpy)]₂AS₄Se₈] were obtained under hydrothermal conditions at 150 °C by treating respectively [MnCl₂(tren)] or [MnCl₂(terpy)] with elemental As and Se at molar ratios of 1:6:12 or 1:4:8 in the presence of the mineralizer Cs₂CO₃. Whereas isolated cyclo-[As₄Se₄]⁴⁻ anions have been structurally characterized in Cs₄As₄Se₈ [31], the ¹⁺[(Mn(tren)]AS₄Se₇⁻⁻] chains of ¹⁺[(Mn(tren)]AS₄Se₇] (see Fig. 6 for the thioarsenate(III) analog) are unknown for binary selenidoarsenates(III) anions. Indeed, these 1D polymeric anions represent the only known example for a selenidoarsenate(III) analog) are unknown for binary selenidoarsenates. This finding correlates with the marked decrease in the tendency of AsE₃⁻⁻ anions to self-condense in the order S > Se > Te.

of the Mn, As and S atoms in ¹⁺{(Mn(terpy)]AS₄Se₈] (Fig. 8). As the {Mn(terpy)]²⁺ fragment is incapable of supporting an E–Mn–E⁻⁻ angle as large as that of 115.6(1)° in the {Mn(terpy)]²⁺ phase, only half of the terminal Se atoms can participate in metal atom coordination (Fig. 10), and the Mn(II) atoms exhibit a distorted trigonal bipyramidal coordination sphere. The ¹⁺[(MnAs₃Se₄] chains of ¹⁺{(Mn(terpy)] AS₄Se₈] can be readily generated from such an arrangement with E = S by simple coordination of the remaining terminal S atoms at the vacant sites of the {Mn(terpy)]²⁺ fragments [48].

Chalcogenidoarsenates(III) Containing Oligochalcogenide Ligands Eₙ⁻⁻ (n = 2–7)

Alkali metal oligochalcogenides are well-known to dissociate into chain anions Eₙ⁻⁻ of various lengths (n = 2–6) in aqueous solution, that are present in dynamic equilibria with one another [2]. Longer oligochalcogenide ions with n > 3 can exist at significant concentrations at low temperatures but are unstable with respect to disproportionation reactions to shorter chain anions Eₙ₋₁⁻⁻ and the chalcogen E at higher temperatures. Although the general tendency of chalcogen atoms to catenate decreases on going down Group 16 from S to Te, many more examples of selenido- and telluridoarsenate anions containing Eₙ⁻⁻ ligands (in particular for n = 2) have been synthesized under mild solvothermal conditions than for thioarsenates. This finding correlates with the marked decrease in the tendency of AsE₃⁻⁻ anions to self-condense in the order S > Se > Te.
Table 3 lists the known binary thio- or selenidoarsenate(III) anions containing oligochalcogenide ligands $E_n^{2−}$ (n = 2, 3, 5, 7). The cyclic anions $[EAsE_5]^{−}$, $[EAsE_7]^{−}$ ($E = S$, Se) and $[As_2E_6]^{2−}$ were all extracted from low-temperature ($T \leq 60$ °C) chalcogen-rich reaction solutions by employing bulky counterions ($Ph_4P^+$, Et$_4N^+$, en$^+$). For instance, (Ph$_4P$)[SAsS$_5$] was obtained by reaction of (Ph$_4P$)[SAsS$_7$] with K$_2$S$_5$ in acetonitrile at r.t. and (Et$_4N$)[SeAsSe$_7$] by heating an alloy of nominal composition °C in ethylenediamine for 8 h and then layering the resulting dark red solution at r.t. with en saturated with (Et$_4N$)Br. The respectively chair- and crown-shaped rings of the $[SeAsSe_5]^{−}$ and $[SeAsSe_7]^{−}$-anions are depicted in Fig. 11 and can be regarded as representing substitution products of the similarly shaped allotropes of selenium, cyclo-$As_2Se_6$ and cyclo-$Se_6$.

The chair-shaped cyclo-$[As_2Se_6]^{2−}$ anion (Fig. 12b) has been obtained both at r.t. and under mild solvothermal conditions (examples for the latter synthetic approach are given for $A = [M(2.2.2-crypt)]^2$, $M = Mn, Fe$ [30]; $A = [Mn(9-aneN$_3$)$_2$] [75]) and has been stabilized in the presence of a wide range of counterions. It is isomeric with the infinite $\frac{1}{2}[AsSe_3]^{3−}$ chains of KAsSe$_3$·H$_2$O and AASSe$_3$·0.5H$_2$O (A = Rb, Cs), which were obtained by hydrothermal reaction of As$_2$Se$_3$ with the appropriate alkali metal carbonate at 135 °C [39]. Although entropy considerations might suggest that condensation of As$_2$Se$_3^{3−}$-anions to corner-bridged species such as cyclo-$[As_2Se_6]^{3−}$ or $\frac{1}{2}[AsSe_2]$ should be favored, the facile oxidative formation of direct Se–Se bonds appears to generate a particularly stable connectivity pattern. It is interesting to note that an analogous As$_2Te_6^{2−}$ anion has also been structurally characterized in (Ph$_4P$)$_2$As$_2Te_6$ [76] and [K(2.2.2-crypt)]$_2$As$_2Te_6$ [77] but that both the analogous [(SAs)$_2(\mu-S_2)_2$]$^{2−}$ and $\frac{1}{2}[AsS_3]$-anions are unknown. However, the isomeric chair-shaped [(SAs)$_2(\mu-S)(\mu-S_3)$]$^{2−}$-anion (Fig. 12a) has been characterized in the compound (Ph$_4P$)$_2$As$_2Se_6$, which was obtained by treating Na$_3$As$_4$ with (Ph$_4P$)Cl in DMF at r.t. [71]. Whereas the endocyclic bond angles in the As$_2Se_6^{2−}$ anion of (Ph$_4P$)$_2$As$_2Se_6$ vary over a wide range between 97.4(1) and 106.5(2)$°$, very little variation (e.g. only 101.0(1)−101.3(1)$°$ in [Na(2.2.2-crypt)]$_2$As$_2Se_6$ [72]) is observed for the ring angles within the As$_2Se_6^{2−}$-anion. In addition, as also found in the $\frac{1}{2}[AsSe^3]$-chains of KAsSe$_3$·H$_2$O and AASSe$_3$·0.5H$_2$O (A = Rb, Cs) [39], rather narrow exocyclic Se–As–Se angles (t = terminal, b = bridging) are present in the latter anion (e.g. 95.1(1) and 96.5(1)$°$ in [Na(2.2.2-crypt)]$_2$As$_2Se_6$ [72]), that are reasonably close to the ideal value of 90° for optimal 4p orbital participation of the Group 15 element in the As–Se bonds. In contrast, much larger Se–As–Se angles between 99.8(1) and 101.6(1)$°$ are found in the As$_2Se_6^{2−}$-anion of (Ph$_4P$)$_2$As$_2Se_6$ [71]. This molecular geometry analysis suggests that the cyclic As$_2Se_6^{2−}$-anions may represent an energetically favorable connectivity pattern.

Although discrete anions of the types $[AsE_2(E_2)]^{3−}$ and $[AsE(E_2)_2]^{3−}$ are unknown, such mononu-
Table 4. Compounds containing thio- or selenidoarsenate(III) ligands with $E_{n}^{2-}$ units ($n = 2, 3$).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$E = S$</th>
<th>$E = Se$</th>
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<tbody>
<tr>
<td>$[\text{AsE}_{2}(E)]^{3-}$</td>
<td>$\text{Cs}<em>2[\text{Sn(AsS}</em>{4})(\text{AsS}_5)]$ [78]</td>
<td>$\text{Cs}<em>2[\text{Sn(AsSe}</em>{4})(\text{AsSe}_5)]$ [78]</td>
</tr>
<tr>
<td></td>
<td>$\text{K}[\text{Sn(AsS}_3)]$ [45]</td>
<td>$\text{In(n}_{2}2(\text{AsSe}_2)]$ en [68]</td>
</tr>
<tr>
<td></td>
<td>$[(\text{C}<em>5\text{Me}</em>{6}\text{Et}_3)\text{CO}_3(\text{AsS}_3)]$ [79]</td>
<td>$[(\text{C}<em>5\text{Me}</em>{6}\text{Et}_3)\text{CO}_3(\text{AsSe}_2)]$ [79]</td>
</tr>
<tr>
<td></td>
<td>$(\text{Ph}_4\text{P})<em>2\text{K}[\text{Pt}</em>{3}(\text{AsS}_3)] 1.5\text{H}_2\text{O}$ [58]</td>
<td></td>
</tr>
<tr>
<td>$[\text{AsE}(E_2)]^{1-}$</td>
<td>$\text{Cs}<em>2[\text{Sn(AsSe}</em>{2})(\text{AsSe}_3)]$ [78]</td>
<td>$\text{Cs}<em>2[\text{Sn(AsSe}</em>{2})(\text{AsSe}_3)]$ [78]</td>
</tr>
<tr>
<td></td>
<td>$[(\text{C}<em>5\text{Me}</em>{6}\text{Et}_3)\text{CO}_3(\text{AsS}_3)]$ [79]</td>
<td>$(\text{Bu}<em>4\text{N})<em>2[\text{MAs}</em>{2}\text{Se}</em>{10}]$ [81]</td>
</tr>
<tr>
<td></td>
<td>$(\text{Ph}_4\text{P})_2[\text{W}<em>2\text{Se}</em>{3}(\text{AsSe}_5)]$ [82]</td>
<td></td>
</tr>
<tr>
<td>$[\text{As}_2\text{E}^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{As}_2\text{E}^{4-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{AsE}^{1-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{AsE}^{2-}$</td>
<td>$(\text{Ph}_4\text{P})_2[\text{Mo}_2\text{O}<em>2\text{S}</em>{2}(\mu-\text{AsS}_2)]$ [84]</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 13. $[\text{AsSe}_{2}(E_2)]^{3-} \text{ and } [\text{AsSe}(E_2)]^{2-} \text{ ligands in (a) }(\text{Ph}_4\text{P})_2[\text{W}_2\text{Se}_{3}(\text{AsSe}_5)]$ [82] and (b) $[(\text{Mn(terpy)})_3(\text{AsSe}_2)]_2$ [81], respectively.

Clear species have been stabilized as ligands in a number of ternary thio- and selenidoarsenate(III) anions. Table 4 lists compounds containing these and other chalcogenidoarsenate(III) ligands with $E_{n}^{2-}$ units ($n = 2, 3$). A variety of synthetic techniques have been employed to obtain such chalcogen-rich compounds including high-temperature fluxes (for $\text{Cs}_2\text{SnAs}_2\text{E}_9$ [78] and $\text{KSnAs}_2$ [45]), extraction from appropriate alloys with ethylenediamine (for $(\text{Ph}_4\text{P})_2\text{K}[\text{Pt}_3(\text{AsS}_3)]$ [58]) and room-temperature reactions of $\text{Cs}_2\text{Sn(AsS}_4)$ [78] and $\text{KSnAsS}_5$ [45], extraction with ethylenediamine (for $(\text{Ph}_4\text{P})_2\text{K}[\text{Pt}_3(\text{AsS}_3)]$ [58]) and room-temperature reactions of $\text{Cs}_2\text{Sn(AsS}_4)$ [78] and $\text{KSnAsS}_5$ [45], extraction with ethylenediamine (for $(\text{Ph}_4\text{P})_2\text{K}[\text{Pt}_3(\text{AsS}_3)]$ [58]) and room-temperature reactions of $\text{Cs}_2\text{Sn(AsS}_4)$ [78] and $\text{KSnAsS}_5$ [45]. It is apparent that employment of starting materials with an overall $E$ : As molar ratio of greater than 3 : 1 is not necessarily a prerequisite for the stabilization of chalcogen-rich arsenate(III) ligands in the coordination sphere of a metal atom. The $[\text{AsSe}_{2}(E_2)]^{3-} \text{ and } [\text{AsE}(E_2)]^{1-} \text{ ligands adopt a chelating mode in all of their complexes with the presence of one or two $E_2$ units enabling the formation of less strained five- or six-membered chelate rings. For instance, the AsSe$_3$$^3-$ ligands adopt an energetically favorable tripodal $\kappa^3\text{Se}_1\text{Se}_4\text{Se}_5$ coordination mode in the compound $(\text{Ph}_4\text{P})_2[\text{W}_2\text{Se}_3(\text{AsSe}_5)]$ [82] (Fig. 13a). Coupled with their ability to form more stable chelate rings, the presence of one or two additional chalcogen atoms will also make the $\text{AsE}_4$$^3-$ and $\text{AsE}_5$$^3-$ anions more electron donating than $\text{AsE}_3$$^3-$ pyramids, which should be preferred by metal atoms in higher oxidation states such as the Sn(IV) atoms in $\text{Cs}_2\text{SnAs}_2\text{E}_9$ and the W(V) atoms in $(\text{Ph}_4\text{P})_2[\text{W}_2\text{Se}_3(\text{AsSe}_5)]$.

$\text{AsE}_4$$^3-$ and $\text{AsE}_5$$^3-$ ligands have also been obtained under mild solvothermal conditions. For instance, $(\text{Ph}_4\text{P})_2\text{K}[\text{Pt}_3(\text{AsS}_4)] 1.5\text{H}_2\text{O}$ was prepared by hydrothermal reaction of $\text{K}_3\text{AsS}_3$ with $(\text{Ph}_4\text{P})\text{Br}$ and $\text{PtCl}_2$ at 110 $^\circ\text{C}$ and contains a trinuclear anion with a central chair-shaped $\text{Pt}_3\text{S}_3$ ring and three tetradentate $\text{AsS}_4$$^3-$ ligands that chelate adjacent Pt atoms in a $\mu_2-\text{1}\kappa^2\text{Se}_1\text{Se}_4\text{Se}_5:2\kappa^2\text{S}_2\text{S}_4$ mode and also bridge these through the terminal bidentate $\text{S}_4$ atoms of their S$_2$ units [58]. A contrasting $\mu_2-1\kappa^2\text{Se}_1\text{Se}_4:2\kappa^2\text{S}_2\text{S}_4$ tridentate bridging mode is adopted by the $\text{AsSe}_3$$^3-$ ligands in the linear trinuclear complex $[(\text{Mn(terpy)})_3(\mu-\text{AsSe}_2)]_2$, whose structure is depicted in Fig. 13b. This compound was prepared by hydrothermal reaction (T = 150 $^\circ\text{C}$) of $[\text{MnCl}_2(\text{terpy})]$ with elemental As and Se at a 1 : 1 : 2 molar ratio in the presence of...
C$_2$CO$_3$ and triethylenetetramine (trien) as mineralizers [81]. It is interesting to note that the employment of tren rather than trien as a solubility enhancer leads instead to the formation of [[Mn(terpy)$_2$]- (µ-As$_2$Se$_4$)$_2$].2H$_2$O [6], which contains a bridging tetradentate As$_2$Se$_4$- ligand with a central As–As bond. The nature of chalcogenidoarsenate(III) ligands stabilized in the Mn(II) coordination spheres of such complexes is also strongly dependent on the geometry of the [Mn(amine)]$^{2+}$ or [Mn(imine)]$^{2+}$ fragment. For instance, reaction of [MnCl$_2$(tren)] with elemental As and Se at a 1:1:2 ratio in superheated H$_2$O/tren (10:1) at $T = 150 \, ^\circ\text{C}$ affords [[Mn(tren)]$_2$(µ-As$_2$Se$_3$)] with bridging dipyramidal As$_2$Se$_5$$^-$ ligands [6], whereas treatment of [MnCl$_2$(cyclam)]Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane) with the elements in the same ratio and at the same temperature in H$_2$O/CH$_3$OH (1:1) yields [[Mn(cyclam)](µ-As$_2$Se$_3$)] (Fig. 14b) with a novel bridging [[As$_2$Se$_2$](µ-As$_2$Se$_3$)]$^{4-}$ ligand [81]. Increasing the [MnCl$_2$(tren)]: As: Se ratio to 1:3:5 and 1:6:12 leads to formation of [[Mn(tren)]$_2$(µ-As$_2$Se$_6$)$_3$] (Fig. 14a) [6] and polymeric $\frac{1}{3}$[[Mn(tren)](As$_2$Se$_7$)]$_n$ [12], respectively. In contrast to the adaptability of the [[Mn(tren)]$^{2+}$ fragment towards chelating ligands or ligand pairs with a wide range of As–Mn–Se angles, the comparatively inflexible [Mn(cyclam)]$^{2+}$ fragment can only support either a trans arrangement of coordinating Se atoms or a tight cis arrangement with a narrow Se–Mn–Se' angle (e.g. 85.60(4)$^\circ$ in [[{Mn(cyclam)}$_2$(µ-As$_2$Se$_6$)]]). A relatively wide Se–Mn–Se' angle of 97.31(6)$^\circ$ is observed in [[{Mn(tren)}$_2$(µ-As$_2$Se$_6$)$_2$]], whose cyclic As$_2$Se$_5$$^-$ dianions can be regarded as being derived from the As$_2$Se$_4$$^-$ tetraanion of [[{Mn(tren)}$_2$(µ-As$_2$Se$_5$)] by addition of the central Se atom of the Se$_3$ unit. Although discrete As$_2$Se$_4$$^-$ anions of this type appear to be unknown, the analogous As$_2$S$_6$$^-$- anion has been characterized in (Ph$_4$P)$_2$As$_2$S$_6$ (Fig. 12a, [71]).

Two tetranuclear chalcogenidoarsenate(III) anions with $E_n$$^-$ units have been described in the literature. The corner-bridged linear As$_4$Se$_1$$^-$ ligands of the hydrothermal phase (Ph$_4$P)$_2$[Hg$_2$As$_4$Se$_7$] [64] contain terminal dumb-bell Se$_2$ units at their first and fourth As atoms and are closely related to the As$_4$Se$_6$$^-$ ligands of the analogous thioarsenate(III) (Ph$_4$P)$_2$[Hg$_2$As$_4$S$_7$] [57]. In contrast, the bridging As$_4$S$_1$$^-$ ligands of (Ph$_4$P)$_2$[Mo$_2$O$_2$S$_2$(µ-As$_4$S$_2$)], which is the product of the reaction of (Ph$_4$P)$_2$Mo$_2$S$_4$ with realgar As$_4$S$_4$ in acetonitrile at r. t. [84] followed by DMF extraction, exhibit a central eight-membered (As$_3$S$_3$)$_2$ ring, whose As atoms are corner-bridged to As$_3$ pyramids. The terminal S atoms of these As$_3$ units coordinate the Mo atoms in four-membered chelate rings.

Whereas [AsTe$_2$(Te$_2$)]$^{3-}$ ligands are known in (n-Bu$_4$N)$_2$[Fe(CO)$_2$(µ-AsTe$_3$)$_2$] [76], (n-Bu$_4$N)$_2$[Cu$_7$Te(AsTe$_4$)$_3$] [85] and the analogous silver cluster anion of (n-Bu$_4$N)$_4$[Ag$_7$Te(AsTe$_4$)$_3$] [80], no examples of coordinating [As$_4$Te$_3$(Te$_2$)$_2$]$^{3-}$ species have been reported.

**Lower Oxidation State Chalcogenidoarsenates**

Chalcogenidoarsenate anions As$_n$E$_x$$^{z-}$ with direct As–As bonds can be classified as either chalcogen-rich (y ≥ x) or chalcogen-poor (y < x). Examples for the former type of anion are provided by the bicyclic anions As$_5$E$_4$$^{z-}$ (E = S, Se), the polymeric selenidoarsenate(II,III) anions $\frac{1}{x}$[As$_4$Se$_6$$^{z-}$] and $\frac{1}{x}$[As$_4$S$_6$$^{z-}$] and the telluridoarsenate(II) anions As$_2$Te$_4$$^{4-}$, $\frac{1}{x}$[As$_2$Te$_5$$^{5-}$], As$_2$Te$_6$$^{4-}$, and cyclo-[As$_7$Te$_6$]$^{4-}$ (Table 5). It is apparent from this list that the lower oxidation state II is more favorable for telluridoarsonates in comparison to S- and Se-containing anions. In contrast, as discussed in Sections 2 and 3, the cyclo-As$_2$Te$_6$$^{2-}$ anion provides the only example of a telluridoarsenate with As in its typical oxidation state III. The stability of the telluridoarsonates(II) is due to the relative weakness of the As–Te bond in comparison to As–As bonds. This weakness is a consequence...
Table 5. Compounds containing telluridoarsenate(II) anions.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{As}_4\text{Te}_3^{4-}$</td>
<td>$\text{As}_2\text{As}_3\text{Te}, A = \text{Na} [89], \text{K} [90] $</td>
</tr>
<tr>
<td>$\text{Rb}_2\text{As}_4\text{Te}_3^{0-}$</td>
<td>$\text{Rb}_2\text{As}_4\text{Te}_3^{0-} - \text{en} [91]$</td>
</tr>
<tr>
<td>$\text{As}_2\text{Te}_5^{2-}$</td>
<td>$(\text{Et}_4\text{N})_2\text{As}_2\text{Te}_5 [92]$</td>
</tr>
<tr>
<td>$\text{As}_2\text{Te}_4^{2-}$</td>
<td>$\text{Cs}_3\text{As}_2\text{Te}_6 [93]$</td>
</tr>
<tr>
<td>cyclo-$\text{As}_4\text{Te}_6^{4-}$</td>
<td>$(\text{Me}_4\text{N})_2\text{As}_4\text{Te}_6 - 2\text{en} [93]$</td>
</tr>
</tbody>
</table>

![Fig. 15](image)

Fig. 15. The contrasting endo-end and exo-end conformations for the $[\text{As}_4\text{E}_6]^{2-}$ anions in (a) $(\text{pipH})_2[\text{As}_4\text{S}_6]$ [86] and (b) $[\text{K}(2.2.2\text{-crypt})]_2[\text{As}_4\text{Se}_6]$ [23], respectively.

of both (a) the poorer overlap between the As 4p orbitals and the more diffuse 5p orbitals of the heavier Te atom and (b) the negligible electronegativity difference between As and Te.

The $\text{As}_4\text{Se}_6^{2-}$ anion has been characterized in $(\text{pipH})_2\text{As}_4\text{S}_6$ (pip = piperidine) [86], $3\text{Rb}_2\text{As}_4\text{S}_6 \cdot \text{As}_4\text{S}_3$ [34], $(\text{Ph}_4\text{P})_2\text{As}_4\text{S}_6$ [87] and $(n\text{-Pr}_2\text{NH})_2\text{As}_4\text{S}_6$ [88] and exhibits the endo-end conformation (Fig. 15a) in all of these compounds. Whereas an endo-exo arrangement has also been established for the analogous $\text{As}_4\text{Se}_6^{2-}$ anion in $(\text{Ph}_4\text{P})_2\text{As}_4\text{Se}_6$ [73], the alternative endo-exo variant (Fig. 15b) has been found in $[\text{K}(2.2.2\text{-crypt})]_2[\text{As}_4\text{Se}_6]$ [23]. Both of these $\text{As}_4\text{Se}_6^{2-}$ anions can be prepared by reducing $\text{As}_4\text{Se}_4$ with potassium, in the former case in DMF in the presence of $(\text{Ph}_4\text{P})\text{Br}$ [73]. Preparation of $(\text{pipH})_2\text{As}_4\text{S}_6$ was achieved in a similar manner by treatment of a solution of realgar in CH$_3$NH(CH$_2$)$_2$OH with piperidine [86]. In contrast to $\text{As}_4\text{Se}_6^{2-}$, compounds containing $\text{As}_4\text{S}_6^{2-}$ anions have also been obtained under mild solvothermal reducing conditions. For instance, $3\text{Rb}_2\text{As}_4\text{S}_6 \cdot \text{As}_4\text{S}_3$ was prepared by hydrothermal reaction of $\text{As}_2\text{S}_3$ with $\text{Rb}_2\text{CO}_3$ at 130 °C [34], and $(n\text{-Pr}_2\text{NH})_2\text{As}_4\text{S}_6$ was isolated after heating an aqueous suspension of elemental As and S to the same temperature in the presence of tripropylamine as the source of the $[n\text{-Pr}_2\text{NH}]^+$ cations [88]. Salts of the cyclo-$[\text{As}_4\text{Se}_6]^{2-}$ anion have often been isolated under similar solvothermal conditions when suitable large mono- or dications were available. This suggests that the bicyclic $\text{As}_4\text{Se}_6^{2-}$ species may represent a thioarsenate counterpart to $\text{As}_2\text{Se}_6^{2-}$ as an energetically favorable cyclic anion of low charge that can serve as an appropriate counterion for a range of bulky organic cations.

As discussed above, hydrothermal reaction of $\text{As}_2\text{Se}_3$ with $\text{A}_2\text{CO}_3$ (A = K, Rb, Cs) leads to the formation of polymeric anions $\text{As}_4\text{Se}_6^{2-}$ in which $\mu$-$\text{AsSe}_3$ tetrahedra are linked by Se–Se bonds [39]. In contrast, metaselenidoarsenate(III) chains $\text{As}_4\text{Se}_6^{2-}$ result when the same starting materials are allowed to react under mild methanolothermal conditions [40]. These contrasting findings prompted a study of the stability of the $\text{As}_4\text{Se}_6^{2-}$ chains or their possible fragment ions cyclo-$[\text{As}_4\text{Se}_6]^{2-}$ in superheated methanol. Would the selenium-rich $\text{As}_4\text{Se}_6^{2-}$ anions disproportionate to highly condensed selenidoarsenate(III) and $\text{Se}_5^{2-}$ anions or alternatively to mixed oxidation state selenidoarsenate(III and IV) and $\text{Se}_5^{2-}$ anions? In fact, heating $\text{CsAsSe}_3 \cdot 0.5\text{H}_2\text{O}$ to 190 °C in methanol leads to the formation of the black selenidoarsenate(II,III) $\text{Cs}_2\text{As}_4\text{Se}_6$ [16] and $\text{Cs}_2\text{Se}_5$ as major products, together with deep-red $\text{Cs}_5\text{As}_5\text{Se}_9$ and red $\text{Cs}_4\text{As}_3\text{Se}_5$ [31] with its cyclo-$[\text{As}_4\text{Se}_6]^{4-}$ anions (Fig. 1b) as accompanying minor products. A plausible stoichiometric equation (5) for the predominant disproportionation reaction can be formulated as follows:

$$4\text{CsAsSe}_3 \rightarrow \text{Cs}_2\text{As}_4\text{Se}_6 + \text{Cs}_2\text{Se}_5 + \text{Se} \quad (5)$$

As depicted in Fig. 16a, the selenidoarsenate(II,III) chains of $\text{Cs}_2\text{As}_4\text{Se}_6$ contain dipyramidal $\text{As}_4\text{Se}_6^{4-}$-building units that share Se atoms with $\text{AsSe}_3^{3-}$ pyramids in five-membered $\text{As}_3\text{Se}_5$ rings and are bridged at the same time by other $\text{AsSe}_3^{3-}$ pyramids into infinite chains. At the time of the original publication [16] in 2006, we failed to recognize that a small quantity of deep-red crystals of a second selenidoarsenate(II,III), $\text{Cs}_3\text{As}_5\text{Se}_9$, was also present in the mixture of reaction products. The novel infinite $\text{As}_4\text{Se}_6^{3-}$ chains of this phase are presented for the first time in this article.
and contain As$_2$Se$_4^{4-}$ units that are linked by corner-sharing linear As$_5$Se$_7^{5-}$ anions (Fig. 16b). Crystallographic details are reported in the Experimental Section at the end of this article.

Two examples have been reported in which As$_2$Se$_4^{4-}$ units act as ligands in ternary selenidoarsenate(II) anions. Such dipyramidal units exhibit a trans conformation in Cs$_4$BiAs$_3$Se$_7$ in which they chelate adjacent Bi atoms of the infinite $\left[\text{Bi(AsSe$_3$)}(\mu$-As$_2$Se$_4)$\right]$_2^{4-}$ chains through Se atoms from different pyramids [15]. A similar trans conformation and an analogous tetradebate coordination mode are also observed for the As$_2$Se$_4^{4-}$ ligands in $\left[\text{Mn(terpy)}\right]_2(\mu$-As$_2$Se$_4)$] [6], whose structure is depicted in Fig. 17. The former compound was prepared by methanolothermal reaction of Li$_3$AsSe$_3$, BiCl$_3$ and Cs$_2$CO$_3$ at 130°C, the latter compound by heating [MnCl$_2$(terpy)], As and Se in H$_2$O/tren (10:1) at 150°C. A unique selenidoarsenate(II,IV) ligand [AsSe$_2$(AsSe$_3$)]$^{5-}$ containing a central As–As bond is present in the $\left[\text{Ag}_2(\mu$-AsSe$_4$)(As$_2$Se$_5$)$\right]^{5-}$ anion of K$_4$Ag$_2$As$_3$Se$_9$ [32], which was also obtained by solvothermal reaction of K$_3$AsSe$_3$ with AgBF$_4$ in superheated methanol at 110°C.

All of the known binary telluridoarsenate(II) anions listed in Table 5 contain the basic dipyrimal As$_2$E$_4^{4-}$ building unit. Isolated As$_2$Te$_4^{4-}$ anions with respectively gauche and trans conformations have been reported for Na$_4$As$_2$Te$_4$ [89] and K$_4$As$_2$Te$_4$ [90]. A trans conformation is also observed for the same anion in Rb$_4$As$_2$Te$_4$·en, which was synthesized by extraction of an alloy of the same nominal composition with ethylenediamine [91]. The related trans-\{$\text{AsTe(Te$_2$)}\}_2^{4-}$ anions of Cs$_4$As$_2$Te$_6$ [93] contain two terminal Te$_2$ dumb-bells and represent the only example of a telluridoarsenate(II) isolated under solvothermal conditions. Whereas this phase can be prepared by methanolothermal reaction of Cs$_2$SO$_3$ with As$_2$Te$_3$ at 145°C, higher temperatures (160–195°C) lead to the isolation of the polytellurides Cs$_2$Te$_5$, Cs$_2$Te$_{13}$, Cs$_4$Te$_{28}$ and Cs$_3$Te$_{22}$ [95, 96], a finding that once again emphasizes the relative weakness of the As–Te bond. Two As$_2$Te$_4^{4-}$ anions are linked together through two shared Te atoms in the chair-shaped cyclo-$\{$As$_4$Te$_6$\}$ anions of (Me$_4$N)$_4$As$_4$Te$_6$.·en [93] and [Ba(en)$_4$]$_2$As$_4$Te$_6$ [94]. The former compound was prepared by electrochemical reduction of an As$_2$Te$_3$ electrode in an ethylenediamine solution of (Me$_4$N)$_4$I. On changing the cation source to (Et$_4$N)$_4$I, $\left[\text{As$_2$Te$_5$}^{2-}\right]$ chains result, in which alternating As$_2$Te$_4^{4-}$ dimers share their four Te atoms with square planar Te$_4^{6-}$ units [92]. No examples of ternary telluridoarsenate(II) anions have been reported.

Chalcogen-poor chalcogenidoarsenates As$_x$E$_y^{z-}$ with $y < x$ always contain more than one direct As–As bond. Cluster anions of the type [As$_{10}$E$_2$]$^{2-}$ are known for E = S–Te and are closely related to the Zintl anion As$_{11}$E$_3^{3-}$ by replacement of one cage As atom by a chalcogen atom and addition of two terminal E atoms. They have been synthesized by reduction of As$_4$E$_4$ (E = S, Se) or As$_2$Te$_3$ with elemental K in NH$_3$ or ethylenediamine in the presence of Ph$_3$P$^+$ (E = Se [97], Te [98]) or [K(2,2,2-crypt)]$^+$ cations (E = S) [23]). The [As$_{11}$Te]$^{3-}$ anion of [K(2,2,2-crypt)$_3$As$_{11}$Te·en] [99] is also related to the tris-homocubane-like As$_{11}$E$_3^{3-}$ anion by addition of a single terminal Te atom. Two selenidoarsenate cluster anions of lower nuclearity ($x = 6, 7$) have been characterized in [Mn(9-ane-N$_3$)$_2$]As$_x$Se$_5$ (9-ane-N$_3$ = 1,4,7-triazacyclononane) [100] and (Ph$_3$P)As$_y$Se$_4$ [101], respectively, and one such anion of higher nuclearity ($x = 12$) in the compound
Fig. 18. The $[\text{As}_6\text{Se}_5]^{2-}$ and $[\text{As}_{12}\text{Se}_4]^{4-}$ cage-like anions of (a) $[\text{Mn}(9\text{-ane-N}_3)_2]\text{As}_6\text{Se}_5$ [100] and (b) $[\text{Co}(\text{NH}_3)_6]_2\text{As}_{12}\text{Se}_4 \cdot 12\text{NH}_3$ [102], respectively.

$[\text{Co}(\text{NH}_3)_6]_2\text{As}_{12}\text{Se}_4 \cdot 12\text{NH}_3$ [102]. The structure of the $[\text{As}_6\text{Se}_5]^{2-}$ anion of $[\text{Mn}(9\text{-ane-N}_3)_2]\text{As}_6\text{Se}_5$, which was prepared by methanolothermal reaction of $[\text{MnCl}_3(9\text{-ane-N}_3)]$ with As$_2$Se$_3$ at 150 °C in the presence of Cs$_2$CO$_3$, is depicted in Fig. 18a. It contains three fused five-membered As$_4$Se$_4$ rings and can be regarded as being related to the bicyclic As$_4$Se$_4$ cage and being bridged by an additional Se atom. Reduction of As$_4$Se$_4$ with Na in liquid ammonia followed by precipitation with CoBr$_2$ affords $[\text{Co}(\text{NH}_3)_6]_2\text{As}_{12}\text{Se}_4 \cdot 12\text{NH}_3$, whose unique cluster anion $[\text{As}_{12}\text{Se}_4]^{4-}$ is shown in Fig. 18b. It consists of a central As$_4$ cage to which four exocyclic, formally negatively charged Se atoms are attached.

**Higher Oxidation State Chalcogenidoarsenates**

Many examples of salts containing isolated tetrahedral thioarsenate(V) anions AsS$_3^{3-}$ have been reported, e.g. Na$_3$AsS$_3 \cdot 8\text{H}_2\text{O}$ [103], K$_3$AsS$_3$ [104], (NH$_4$)$_3$AsS$_3$ [105], and Ba$_3$(AsS$_3$)$_2 \cdot 7\text{H}_2\text{O}$ [106]. The analogous AsSe$_3^{3-}$ anion has been characterized in [Li(NH$_3$)$_4$]AsSe$_4$ [107], Na$_3$AsSe$_3 \cdot 9\text{H}_2\text{O}$ [108], Rb$_3$AsSe$_4$, Cs$_3$AsSe$_4$ [109], and Cs$_3$AsSe$_4 \cdot \text{H}_2\text{O}$ [110] among other compounds. The tetraselenidoarsenate(V) salts of the heavier alkali metal cations Rb$^+$ and Cs$^+$ were obtained by methanolothermal reaction of $\text{A}_2\text{CO}_3$ (A = Rb, Cs) with As$_2$Se$_3$ and Se at an appropriate molar ratio [109]. On changing the solvent from methanol to an equimolar H$_2\text{O}/\text{CH}_3\text{OH}$ mixture the monohydrate Cs$_3$AsSe$_4 \cdot \text{H}_2\text{O}$ [110] is formed, rather than Cs$_3$AsSe$_4$. Reaction of the solvent with the thio- or selenidoarsenate(III) anions AsE$_3^{3-}$ present in methanolothermal reaction solutions affords substituted chalcogenidoarsenate(V) anions of the types $[\text{As}(\text{CH}_3)]E_3^{2-}$ ($E = \text{S}$ [111], Se [16]) and $[\text{As}(\text{CH}_3)_2]\text{Se}_2^{2-}$ [112] on leaving the mother liquor to slowly evaporate. The formation of $[\text{As}(\text{CH}_3)]E_3^{2-}$ anions requires methanol reduction according to (6):

$$\text{AsE}_3^{3-} + \text{CH}_3\text{OH} \rightleftharpoons [\text{As}(\text{CH}_3)]E_3^{2-} + \text{OH}^- \quad (6)$$

Pertinent examples of other substituted selenidoarsenate(V) anions are found in the salts $[\text{K}(\text{2.2.2-crypt})]_2 - [\text{As}(\text{CH}_3\text{CN})\text{Se}_3]$ [113] and (pipH)$_2[\text{AsPh}_2\text{Se}_2]$ [114]. As to be expected, the potential telluridoarsenate(V) anion AsTe$_3^{3-}$ is unknown.

Tetrahedral AsS$_3^{3-}$ ligands have been incorporated into the ternary coinage metal thioarsenate(V) polyanions of compounds such as NH$_4[\text{Ag}_2\text{AsS}_4]$ [115], (NH$_3$)$_2\text{CH}_2\text{CH}_2\text{NH}_3[\text{AgAsS}_4]$ [116], K[Ag$_2$AsS$_4$] [117], Cs$_2[\text{AgAsS}_4]$ [118], and K$_2[\text{AuAsS}_4]$ [119]. Rb$_8[\text{Cd}_2(\text{AsS}_4)_2(\mu-\text{AsS}_3)_2]$ was obtained from a rubidium polythioarsenate flux at 500 °C [120] and contains a dinuclear anion in which the Cd atoms are bridged by a unique tetradentate $[\text{As}_3(\text{S}_2)]^{3-}$ ligand. The $[\text{Mn}_2(\text{AsS}_4)_2(\mu-\text{AsS}_3)_2]^{3-}$ anions of the similarly prepared compounds $\text{As}[\text{Mn}_2\text{As}_4\text{S}_{16}]$ (A = Rb, Cs) [120] exhibit a comparable dinuclear structure but in this case $\text{AsS}_3^{3-}$ ligands exhibit adequate bite angles to allow the bridging of the smaller Mn atoms in an analogous $\mu-\text{S}_2\text{S}_1\text{S}_2 : 2\text{S}_3 : 2\text{S}_4 : \text{S}_4$ mode. Examples have also recently been reported of AsS$_3^{3-}$ anions acting as ligands to $[\text{Mn}(\text{amine})]^{2+}$ and $[\text{Mn}(\text{imine})]^{2+}$ fragments in hydrothermally synthesized compounds, and to lanthanide metals in the phases K$_3[\text{Ln(AsS}_4)\text{$_2$}]$ ($\text{Ln} = \text{Nd, Sm, Gd}$) [121], which were obtained in potassium thioarsenate fluxes. The tetrathioarsenate(V) anion adopts a chelating mode in the anion of $[\text{Mn(en)}_2]_2[\{}[\text{Mn(en)}_2]_2\text{As}_2\text{[AsS}_6\text{]}_2$ [13], a bridging $\mu_2-1\text{S}_1\text{S}_2 : 2\text{S}_3 : 2\text{S}_4$ mode in the infinite chains of $[\text{Mn(dien)}]_2[\{}[\text{Mn(dien)}]_2\text{[AsS}_4\text{]}_2 \cdot 4\text{H}_2\text{O}$ [13] and a hexadentate $\mu_2-1\text{κ}_1\text{κ}_1\text{S}_1\text{S}_2 : 2\text{κ}_1\text{κ}_1\text{S}_3 : 3\text{κ}_0\text{κ}_3\text{S}_4$ mode in the 1D polyanions of $[[\text{Mn}(\text{2,2-bpy})]_2(\mu_2-\text{AsS}_3)_2] \cdot \text{H}_2\text{O}$ [5]. A $\mu_3-\text{AsS}_3^{3-}$ bridging ligand has been observed in the lanthanide thioarsenates K$_3[\text{Ln(AsS}_4)\text{$_2$}]$ [121].

In striking contrast to the ternary thioarsenate(V) anions, very few examples of compounds containing AsSe$_3^{3-}$ ligands have been reported. However, $\mu_2$-bridging AsSe$_3^{3-}$ ligands are present in the $\text{As}[\text{As}(\text{SeS}_3)_2]$ layers of the methanolothermal phase K$_2[\text{As}_3\text{Se}_6\text{O}_8]$ [32], which also contain the mixed valent As$_3\text{Se}_4^{4-}$ anion, already discussed in Section 4. A $\mu_2-1\text{κ}_0\text{κ}_1\text{Se}_1\text{Se}_2 : 2\text{κ}_0\text{κ}_1\text{Se}_3$ mode is adopted by the tetrahedral selenidoarsenate(V) ligand in the infinite chains of the lanthanide compounds $\text{Ln}(\text{dien})_2(\mu_2-\text{AsS}_3)$ ($\text{Ln} = \text{Nd, Sm}$) [122], which...
were synthesized by reaction of As$_2$O$_3$ with Se and Nd$_2$O$_3$ or Sm$_2$O$_3$ in dien at 140 °C. We now report the first example of a transition metal complex containing an AsSe$_4^{3-}$ ligand. Cs$_2$[Mn(terpy)]AsSe$_4$ · CH$_3$OH was obtained in low yield by methanolothermal reaction of MnCl$_2$, trien, As and Se in the presence of Cs$_2$CO$_3$ at 150 °C and contains a bidentate AsSe$_4^{3-}$ ligand (Fig. 19). The four-membered chelate ring exhibits a narrow Se–Mn–Se′ ligand (Fig. 19). The four-membered chelate ring exhibits a narrow Se–Mn–Se′ ligand (Fig. 19). The four-membered chelate ring exhibits a narrow Se–Mn–Se′ ligand (Fig. 19). The four-membered chelate ring exhibits a narrow Se–Mn–Se′ ligand (Fig. 19). The four-membered chelate ring exhibits a narrow Se–Mn–Se′ ligand (Fig. 19).

Conclusions

Despite the structural restrictions imposed by the reluctance of trivalent arsenic to extend its coordination sphere, employment of mild solvothermal preparation conditions has led to the characterization of a remarkable variety of chalcogenidoarsenate anions. This is due, in part, to the ready formation of homonuclear As–As and E–E bonds in building units of the types As$_2$E$_4^{4-}$ and [AsE$_2$(E$_2$)]$^{3-}$, respectively. Although many isostructural binary anions are known for the thio- and selenidoarsenates(III) (see Tables 1 and 3), a number of striking differences are also apparent.

a) The simple thioarsenate(III) anions AsS$_3^{3-}$, As$_2$S$_4^{4-}$, and cyclo-[As$_5$S$_6$]$^{3-}$ exhibit a far greater tendency to self-condense to afford polymeric anions than their selenidoarsenate(III) counterparts.

Whereas alkali metal and alkylammonium thioarsenates(III) of the types AAs$_2$S$_2$, A$_2$As$_3$S$_7$, A$_2$As$_5$S$_{10}$ and A$_2$As$_8$S$_{15}$ (Table 2) with condensation grades c of 0.50–0.615 have been obtained under mild solvothermal conditions, the only known binary polyselenidoarsenate(III) anion is $\frac{1}{6}$[AsSe$_2^{3-}$] found in the alkali metal phases AAsSe$_2$ (A = Na–Cs). The polymeric $\frac{1}{6}$[As$_4$Se$_7^{2-}$] ligands of $\frac{1}{6}$[Mn(terpy)]As$_4$Se$_7$ [12] with their condensation grade of c = 0.571 represent the only example of a selenidoarsenate(III) anion with c greater than 0.50.

b) In contrast to the binary selenidoarsenate(III) anions $\frac{1}{6}$[AsSe$_3^{3-}$] and cyclo-[As$_2$Se$_6$]$^{2-}$, no thioarsenate(III) anions containing AsE$_3^{3-}$ pyramids linked by homonuclear E–E bonds are currently known.

Infinite $\frac{1}{6}$[AsSe$_3^{3-}$] chains have been characterized in the hydrothermally synthesized phases KAsSe$_3$ · H$_2$O and AAsSe$_3$ · 0.5H$_2$O (A = Rb, Cs) [39]. The chair-shaped cyclo-[As$_2$Se$_6$]$^{2-}$ anions have been isolated both at r.t. and under mild solvothermal conditions in the presence of a variety of bulky counterions such as Et$_4$N$^+$ [68], Ph$_4$P$^+$ [69, 73] and [M(en)$_3$]$^{2+}$ (M = Mn, Fe) [30].

c) Whereas the As$_4$S$_6^{2-}$ anion represents the only currently known example of a thioarsenate species with a homonuclear As–As bond, not only the analogous As$_4$Se$_6^{2-}$ anion but also a variety of other binary and ternary selenidoarsenates containing the characteristic As$_2$E$_4^{4-}$ unit have been prepared.

The dipyramidal selenidoarsenate(III) moiety As$_2$S$_4$E$_4^{4-}$ has been characterized as a building unit in the $\frac{1}{6}$[As$_4$Se$_6^{2-}$] and $\frac{1}{6}$[As$_5$Se$_9^{5-}$] chains of Cs$_2$As$_4$Se$_6$ [16] and Cs$_5$As$_5$Se$_9$, respectively, and as a tetradeinate $\mu_2$-1K$^2$Se$_1$Se$_1 : 2K$^2$Se$_2$Se$_4$ ligand in Cs$_8$BiAs$_4$Se$_7$ [15] and {[M(neterpy)]$_2$As$_2$Se$_4$} [6].

These differences result in general from the decrease in the bond strength of the heteronuclear As–E bond on going from S to Se. The underlying trend towards anions with homonuclear E–E and/or As–As bonds is even more apparent on descending Group 16 further to E = Te. Pyramidal AsTe$_3^{3-}$ is unknown as an isolated anion or ligand, as are anions containing As–Te–As linkages. The only known telluridoarsenate(III) anion is the chair-shaped cyclo-[As$_5$Te$_6$]$^{2-}$ anion of (Ph$_3$P)$_2$As$_2$Te$_6$ [76] and [K(2,2,2-crypt)$_2$]$_2$As$_2$Te$_6$ [77] with its AsTe$_3^{3-}$ units linked by Te–Te bonds. In contrast, the dipyramidal As$_2$Te$_4^{4-}$ species has been characterized not only as a discrete anion in alkali metal salts A$_4$As$_2$Te$_4$ (A = Na–Rb [89–91]) but also as a building unit in the binary $\frac{1}{6}$[As$_2$Te$_5^{2-}$], As$_5$Te$_6^{3-}$ and cyclo-[As$_6$Te$_6^{5-}$] anions [92–94]. Of these, the infinite $\frac{1}{6}$[As$_2$Te$_5^{2-}$] chain of (Et$_4$N)$_2$As$_2$Te$_5$ and the dinuclear trans-{$\{[AsTe(Te$_2$)$_2}$]$_2$]$^{2-}$ anion of Cs$_4$As$_2$Te$_6$ appear to represent the only examples of chalcogenidoarsenate species simultaneously displaying As–E, As–As and E–E bonds.
Experimental Section

Cs₂As₅Se₉

300 mg CsAsSe₃ · 0.5H₂O (0.66 mmol) [39] was heated to 190 °C in methanol (0.4 mL) in a sealed glass tube. After 30 h the contents was allowed to cool to r. t. at 2 °C/h to afford deep-red crystals of Cs₂As₅Se₉ in about 3 % yield (relative to As) together with black Cs₂As₂Se₆ [16] (32 %), red Cs₂As₃Se₅ [31] (10 %) and black Cs₂Se₅. Crystals of Cs₂As₅Se₉ were separated under a polarizing microscope. Cs₂As₅Se₉ (M = 1749.8 g mol⁻¹) crystallizes in the orthorhombic space group Pnma (no. 62) with a = 7.954(2), b = 27.031(5), c = 12.276(3) Å, V = 2639.5(9) Å³, Z = 4, Dₐcalc = 4.40 g cm⁻³, μ = 24.5 mm⁻¹, F(000) = 2984 e. Intensity data were collected on a Siemens P4 diffractometer in the ω scan mode at 292(2) K for a crystal of size 0.15 × 0.11 × 0.10 mm³ using graphite-monochromated MoKα radiation (λ = 0.71073 Å) and corrected in a semi-empirical manner for absorption (ψ scans). The structure was solved by Direct Methods and refined for 91 parameters against |F| ≥ 2σ(|F|) and ωF² = 0.321 for all 2371 symmetry-independent reflections (0 ≤ h ≤ 32, 0 ≤ k ≤ 14, 0 ≤ l ≤ 14) from 2371 measured reflections. All non-hydrogen atoms were assigned anisotropic displacement parameters. The residual electron density values were 2.02 and 2.71 e Å⁻³.

Cs[ Mn(trien)][AsSe₄] · CH₃OH

79.3 mg of Se (1.0 mmol), 37.6 mg of As (0.5 mmol), 63.4 mg of MnCl₂ (0.5 mmol), 0.075 mL of trien (0.5 mmol) and 165.0 mg of Cs₂CO₃ (0.5 mmol) were tempered in 1.0 mL methanol in a sealed glass tube at 150 °C for 25 h. Slow cooling to r. t. at 1 °C/h afforded orange crystals of Cs[(Mn(trien))[AsSe₄]] · CH₃OH in low yield (5 %). CsH₂₂AsCsMn₄O₆Se₄ (M = 756.9 g mol⁻¹) crystallizes in the monoclinic space group P2₁/n (no. 14) with a = 7.968(2), b = 11.359(5), c = 22.110(6) Å, β = 95.74(1)°, V = 1991.3(12) Å³, Z = 4, Dₐcalc = 2.53 g cm⁻³, μ = 11.4 mm⁻¹, F(000) = 1396 e. Intensity data were collected on a Siemens P4 diffractometer in the ω scan mode at 292(2) K for a crystal of size 0.45 × 0.26 × 0.23 mm³ using graphite-monochromated MoKα radiation (λ = 0.71073 Å) and corrected using ψ scans for absorption. The structure was solved by Direct Methods and refined for 122 parameters against F₀² using SHELX-97 [123] to R₁ = 0.075 [I ≥ 2σ(I)] and wR₂ = 0.253 for all 3467 symmetry-independent reflections (−1 ≤ h ≤ 9, −13 ≤ k ≤ 1, −26 ≤ l ≤ 26) from 4693 measured reflections. All non-hydrogen atoms were assigned anisotropic displacement parameters, and H atoms were refined with a riding model. The residual electron density values were 1.66 and 2.47 e Å⁻³.

CSD 421375 (Cs₂As₅Se₉) and CCDC 761656 (Cs[ Mn(trien)][AsSe₄]) · CH₃OH contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen or The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


