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 $\mathrm{As}_xE_y{}^{z-}$ 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 $\mathrm{Cs_3AsGeSe_5}$ and polymeric selenidoarsenates(II, III) such as $\mathrm{Cs_2As_4Se_6}$. A currently expanding area of interest involves the employment of transition metal-polyamine or -polyimine fragments such as $\{\mathrm{Mn(tren)}\}^{2+}$ or $\{\mathrm{Mn(terpy)}\}^{2+}$ as structure-directing agents. The metal atoms of such cations can be connected to the terminal chalcogen atoms of oligomeric or polymeric anions $\mathrm{As}_xE_y{}^{z-}$ 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*-$[\mathrm{As_4S_8}]^{4-}$, $\mathrm{As_2Se_6}^{2-}$, $\mathrm{As_2Se_6}^{4-}$ and $^{1}_{\infty}[\mathrm{As_4Se_7}^{2-}]$. The syntheses and structures of the new compounds $\mathrm{Cs_5As_5Se_9}$ and $\mathrm{Cs[\{Mn(trien)\}(AsSe_4\text{-}\kappa^2Se)] \cdot CH_3OH}$ are also presented. Whereas the former phase contains infinite selenidoarsenate(II,III) chains $^{1}_{\infty}[\mathrm{As_5Se_9}^{5-}]$, the $[\{\mathrm{Mn(trien)}\}(\mathrm{AsSe_4})]^-$ 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

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 $\mathrm{H_2O}$ [2], $\mathrm{CH_3OH}$ [3], $\mathrm{NH_3}$ [2], en (= ethylenediamine) [4], dien (= diethylenetriamine) [5], tren (= tris(2-aminoethyl)amine) [6], and $\mathrm{CH_3CN}$ [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 reluctancy to adopt hypervalent coordination polyhedra in its chalcogenido anions. To our knowledge, relatively undistorted ψ-$\mathrm{As}E_4$ (E = S, Se, Te) trigonal bipyramids have only been reported for the double chains $^{1}_{\infty}[\mathrm{As_6S_{10}}^{2-}]$ of $\mathrm{(Me_4N)_2As_6S_{10}}$ [7]. In this and other relevant coordination polyhedra (*i. e.* ψ-ME_3 tetrahedra and ψ-ME_5 octahedra) of trivalent Group 15 elements M, use of the Greek letter ψ implies that one site is formally occupied by a non-bonded electron pair. The effective

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

Anion	E = S	E = Se
AsE_3^{3-}	A_3AsS_3 A = Li [18], Na, K [19] $Ba_2As_2S_5$ [20]	A_3AsSe_3 A = Na, K [21] $Ba_2As_2Se_5$ [22]
cis-$[As_2E_4]^{2-}$	$[K(2.2.2\text{-crypt})]_2(As_2S_4) \cdot 2\,CH_3CN$ [23]	
trans-$[As_2E_4]^{2-}$	$Ba_2As_2S_5$ [20]	$Ba_2As_2Se_5$ [22]
$As_2E_5^{4-}$	$[M(en)_3]_2As_2S_5$ M = Mn, Ni [24]	$[M(en)_3]_2As_2Se_5$ M = Mn [24], Co [25]
cyclo-$[As_3E_6]^{3-}$	$[enH_2]_3(As_3S_6)_2 \cdot 6en$ [26] $[Fe(phen)_3]As_3S_6 \cdot dien \cdot 7H_2O$ [27], refs. [13, 28][a]	$[Sr(en)_4]_2(As_3Se_6)Cl$ [29] $[Mn(dien)_2]_3(As_3Se_6)_2$ [30]
cyclo-$[As_4E_8]^{4-}$		$Cs_4As_4Se_8$ [31]

[a] Ref. [13]: $[Mn(en)_3]_2[\{Mn(en)_2\}AsS_4]As_3S_6$; ref. [28]: $[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6 \cdot 2NH_3$ and $[NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6 \cdot NH_3$.

restriction to ψ-AsE_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_n^{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 $\{Mn(dien)\}^{2+}$, $\{Mn(tren)\}^{2+}$ or $\{Mn(terpy)\}^{2+}$ (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 $^1_\infty[\{Mn(tren)\}(As_4Se_7)]$ contains $^1_\infty[As_4Se_7^{2-}]$ 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 $^1_\infty[MnAsS_4^-]$ chains of $[Mn(dien)_2][\{Mn(dien)\}(\mu\text{-}AsS_4)]_2 \cdot 4H_2O$ [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 $Cs_3AsGeSe_5$ [14] and $Cs_4BiAs_3Se_7$ [15] and the isolation of novel binary lower oxidation state selenidoarsenates such as the $^1_\infty[As_4Se_6^{2-}]$ chain anions of $Cs_2As_4Se_6$ [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, $Cs_5As_5Se_9$ and $Cs[\{Mn(trien)\}(AsSe_4\text{-}\kappa^2Se)] \cdot CH_3OH$ (trien = triethylenetetramine). Whereas the former phase contains a mixed oxidation state $^1_\infty[As_5Se_9^{5-}]$ chain, the $[\{Mn(trien)\}AsSe_4]^-$ 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_2S_3 dissolves in aqueous alkaline solution to afford ψ-tetrahedral AsS_3^{3-} anions together with oxo- and oxothio-anions. UV/Vis spectroscopic and potentiometric studies [17] have shown that mononuclear AsS_3^{3-} anions readily condense to corner-bridged dipyramidal $As_2S_5^{4-}$ and cyclic tripyramidal $As_3S_6^{3-}$ anions, of which the latter species predominate at pH $\leq$ 11. Both $As_2E_5^{4-}$ [24, 25] and *cyclo*-$As_3E_6^{3-}$ [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 $[Fe(phen)_3]As_3S_6 \cdot dien \cdot 7H_2O$ [27] from a dien/water mixture containing $FeCl_3$, phen,

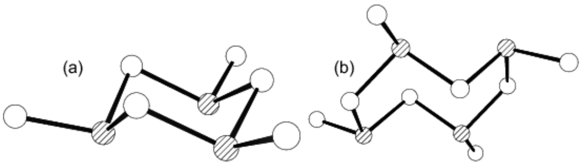
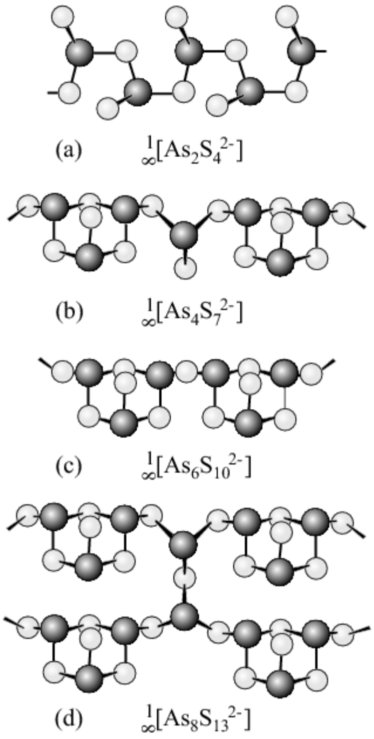


Fig. 1. The *cyclo*-$[As_3Se_6]^{3-}$ and *cyclo*-$[As_4Se_8]^{4-}$ anions of (a) $[Sr(en)_4]_2(As_3Se_6)Cl$ [29] and (b) $Cs_4As_4Se_8$ [31]. In this and Figs. 5 – 19, shaded circles represent As atoms, cross-hatched circles metal atoms, and open large circles S and Se atoms.

As_2O_3 and S (molar ratio 1 : 3 : 2 : 6) at 140 °C. An analogous solvothermal strategy was employed for the preparation of the complexes $[M(en)_3]_2As_2E_5$ (E = S, M = Mn, Ni; E = Se, M = Mn, Co) [24,25] and $[Mn(dien)_2]_3(As_3Se_6)_2$ [30], which were synthesized from As_2O_3 and the appropriate chalcogen E and metal chloride MCl_2 in respectively en and dien reaction solutions at T = 140 °C. In contrast, the cyclic $As_3E_6{}^{3-}$ anions of $[enH_2]_3(As_3S_6)_2 \cdot 6en$ [26] and $[Sr(en)_4]_2(As_3Se_6)Cl$ [29] (Fig. 1a) were obtained directly by dissolving respectively As_2S_3 or As_2Se_3 in refluxing ethylenediamine, in the latter case in the presence of $SrCl_2$ to afford the suitable complex cation $[Sr(en)_4]^{2+}$. The more polar terminal As–E_t bonds in these $As_3E_6{}^{3-}$ and other chalcogenidoarsenate anions are significantly shorter than the accompanying bridging As–E_b bonds. The differences are exemplified by the As–S_t and As–S_b distances of 2.153 – 2.159 and 2.274 – 2.314 Å, respectively, in $[enH_2]_3(As_3S_6)_2 \cdot 6en$ and the As–Se_t and As–Se_b bond lengths of 2.288–2.296 Å and 2.398–2.424 Å in $[Sr(en)_4)]_2(As_3Se_6)Cl$. Interestingly, the cage-like As(II) sulfide, realgar As_4S_4, was employed as the source for both the edge-bridged *cis*-$[As_2S_4]^{2-}$ anions in $[K(2.2.2\text{-crypt})]_2As_2S_4 \cdot 2CH_3CN$ [23] and the corner-bridged $As_3S_6{}^{3-}$ anions of $[NH_4(NH_3)_4][Ca(NH_3)_7]As_3S_6 \cdot 2NH_3$ and $[NH_4(NH_3)_4][Ba(NH_3)_8]As_3S_6 \cdot NH_3$ [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 anion 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*-$[As_4Se_8]^{4-}$ anion (Fig. 1b) of $Cs_4As_4Se_8$ [31], which was obtained as a by-product of the disproportionation reaction of the $^1_\infty[\{AsSe(\mu\text{-}Se_2)\}^-]$ chains of $CsAsSe_3 \cdot 0.5H_2O$ to the mixed oxidation state selenidoarsenate(II,III) $Cs_2As_4Se_6$ [16] and the polyselenide Cs_2Se_5 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 $AsE_3{}^{3-}$ (E = S, Se) anions have been structurally characterized in the phases Li_3AsSe_3 [18], A_3AsE_3 (A = Na, K) [19,21] and $Ba_2As_2E_5$ [20,22], all of which were first prepared in high temperature fluxes, *e. g.* in the case of Na_3AsS_3 by tempering a mixture of Na_2S, As and S in a sealed glass tube at 420 °C for 10 d [19b]. However, the potassium compounds K_3AsE_3 (E = S, Se) have also been obtained as brown powders on evaporation of ammonia solutions containing stoichiometric quantities of K, As_2E_3 and E [32].

The reluctancy 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 $AsS_3{}^{3-}$, $As_2S_5{}^{4-}$ or *cyclo*-$[As_3S_6]^{3-}$ under mild solvother-


(a) $^1_\infty[As_2S_4{}^{2-}]$

(b) $^1_\infty[As_4S_7{}^{2-}]$

(c) $^1_\infty[As_6S_{10}{}^{2-}]$

(d) $^1_\infty[As_8S_{13}{}^{2-}]$

Fig. 2. Potential chain anions $^1_\infty[\{As_{2x}S_{3x+1}\}^{2-}]$, x = 1 – 4, resulting from the corner-bridged condensation of linear $[As_xS_{2x+1}]^{(2+x)-}$ anions (x = 1 or 2) and/or *cyclo*-$[As_3S_6]^{3-}$ anions.

Table 2. Alkali and alkylammonium thioarsenates(III) of the family $A_2[\mathrm{As}_{2x}\mathrm{S}_{3x+1}]$.

Nuclearity $2x$	Condensation grade c[a]	Cations A	References
2	0.50	Na,Rb	[33, 34]
4	0.571	$\mathrm{Me_4N}$	[7]
6	0.60	$\mathrm{Me_4N}$, $\mathrm{Et_4N}$	[7, 35]
8	0.615	$A(\mathrm{H_2O})$, A = K, Rb, $\mathrm{NH_4}$	[36]
		Cs, $\mathrm{Et_4N}$	[37, 35]

[a] $c = 2x/(3x+1)$.

mal conditions might be expected to generate a family of structurally related polymeric chain anions $^1_\infty[\{\mathrm{As}_{2x}\mathrm{S}_{3x+1}\}^{2-}]$ (x = 1 – 4), whose connectivity patterns are illustrated in Fig. 2. As listed in Table 2, 1D thioarsenates(III) of the formula types $A_2[\mathrm{As}_{2x}\mathrm{S}_{3x+1}]$ 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 $A\mathrm{AsS_2}$ (type *a*, A = Na, Rb [33, 34]), $A_2\mathrm{As_4S_7}$ (type *b*, A = $\mathrm{Me_4N}$ [7]), $A_2\mathrm{As_8S_{13}}$ (type *d*, A = $\mathrm{Et_4N}$ [35]), and $A_2\mathrm{As_8S_{13}} \cdot \mathrm{H_2O}$ (type *d*, A = K, Rb, $\mathrm{NH_4}$ [36]), modified connectivity patterns (Fig. 3) were established for the $^1_\infty[\mathrm{As_6S_{10}}^{2-}]$ anions of $(\mathrm{Me_4N})_2\mathrm{As_6S_{10}}$ [7] and $(\mathrm{Et_4N})_2\mathrm{As_6S_{10}}$ [35]. The *zweier* repeating units depicted for the metathioarsenate(III) chains $^1_\infty[\mathrm{As_2S_4}^{2-}]$ of type *a* in Fig. 2 are observed in $\mathrm{NaAsS_2}$, but *vierer* chains are present in $\mathrm{RbAsS_2}$. In contrast to $\mathrm{NaAsS_2}$, which was prepared by heating $\mathrm{As_2S_3}$ in an $\mathrm{Na_2S}$ flux at 220 °C, $\mathrm{RbAsS_2}$ was isolated together with the phase $3\mathrm{Rb_2As_4S_6} \cdot \mathrm{As_4S_3}$ by methanolothermal reaction of $\mathrm{Rb_2CO_3}$ with orpiment $\mathrm{As_2S_3}$ for 7 d in the temperature range 130 – 180 °C [34]. Employment of the same starting materials, $\mathrm{Rb_2CO_3}$ and $\mathrm{As_2S_3}$, under hydrothermal conditions (T = 200 °C, 7 d) led to the formation of the more highly condensed $^1_\infty[\mathrm{As_8S_{13}}^{2-}]$ chains of $\mathrm{Rb_2As_8S_{13}} \cdot \mathrm{H_2O}$. The isostructural phases $A_2\mathrm{As_8S_{13}} \cdot \mathrm{H_2O}$ with A = K, $\mathrm{NH_4}$ were obtained in a similar manner [36]. The alkali metal carbonates $A_2\mathrm{CO_3}$ (A = 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 $\mathrm{CO_2}$.

$$3\,\mathrm{CO_3}^{2-} + \mathrm{As_2}E_3 \rightleftharpoons \mathrm{As}E_3{}^{3-} + \mathrm{AsO_3}^{3-} + 3\,\mathrm{CO_2} \quad (1)$$

The contrasting products for the hydrothermal and methanolothermal reactions of $\mathrm{Rb_2CO_3}$ with $\mathrm{As_2S_3}$ highlight two general aspects of the solvothermal synthesis of thioarsenate anions. Firstly, the greater tendency of water to self-ionize [pK_auto($\mathrm{CH_3OH}$)–pK_auto($\mathrm{H_2O}$) = 3.2] [38] favors the formation of highly condensed polyanions as in reaction (2) by providing more protons to remove the resulting S^{2-} anions as HS^-.

$$2\,\mathrm{As_3S_6}^{3-} + \mathrm{As_2S_5}^{4-} \rightleftharpoons \frac{1}{n}[\mathrm{As_8S_{13}}^{2-}]_n + 4\,\mathrm{S}^{2-} \quad (2)$$

Secondly, employment of alkali metal carbonates can also lead to the concomitant formation of reduction products such as the $\mathrm{As_4S_6}^{2-}$ anions and the dimorphite $\mathrm{As_4S_3}$ molecules of $\mathrm{Rb_2As_4S_6} \cdot \mathrm{As_4S_3}$. A thermodynamically plausible stoichiometric reaction (3) can be formulated for the methanolothermal reaction of $\mathrm{Rb_2CO_3}$ and $\mathrm{As_2S_3}$ as follows:

$$\begin{aligned} &24\,\mathrm{Rb_2CO_3} + 35\,\mathrm{As_2S_3} \\ &\rightleftharpoons 3\,[3\,\mathrm{Rb_2As_4S_6} \cdot \mathrm{As_4S_3}] + 18\,\mathrm{RbAsS_2} \qquad (3) \\ &\quad + 4\,\mathrm{Rb_3AsO_3} + 24\,\mathrm{CO_2} + 6\,\mathrm{SO_2} \end{aligned}$$

Whereas the alkylammonium thioarsenates(III) $(\mathrm{Me_4N})_2\mathrm{As_4S_7}$ and $(\mathrm{R_4N})_2\mathrm{As_6S_{10}}$ (R = Me, Et) may be prepared under very mild solvothermal conditions by treatment of $\mathrm{As_2S_3}$ with $\mathrm{Na_2S}$ in the presence of $(\mathrm{R_4N})\mathrm{Cl}$ in acetonitrile at 110 °C [7, 35], much more forcing hydrothermal conditions (T = 180 °C) are required to obtain the highly condensed phase $(\mathrm{Et_4N})_2\mathrm{As_8S_{13}}$ from such starting materials. Alternating corner bridging of *cyclo*-$[\mathrm{As_3S_6}]^{3-}$ and pyramidal $\mathrm{AsS_3}^{3-}$ anions generates the $^1_\infty[\mathrm{As_4S_7}^{2-}]$ chains (Fig. 2, type *b*) of $(\mathrm{Me_4N})_2\mathrm{As_4S_7}$. Although the direct linkage of *cyclo*-$[\mathrm{As_3S_6}]^{3-}$ anions (Fig. 2, type *c*) is clearly recognizable in the $^1_\infty[\mathrm{As_6S_{10}}^{2-}]$ anions of $(\mathrm{Me_4N})_2\mathrm{As_6S_{10}}$ (Fig. 3a), these individual chains are joined together into double chains through planar $\mathrm{As_2S_2}$ rings, whose arsenic atoms exhibit relatively undistorted ψ-trigonal bipyramidal coordination geometries. Contrasting bond lengths of 2.533(3) and 2.202(2) Å are observed for the respectively axial and equatorial As–S bonds within the four-membered rings. In contrast, one half of the potential $\mathrm{As_3S_3}$ rings in the related $^1_\infty[\mathrm{As_6S_{10}}^{2-}]$ double chains of $(\mathrm{Et_4N})_2\mathrm{As_6S_{10}}$ (Fig. 3b) appear to have opened to afford linear bridging units $\mathrm{As_3S_7}^{5-}$. A relationship between the size of the counter cation and the condensation grade c (c = $2x/(3x+1)$) of the resulting polyanion (*e. g.* c = 0.50 for Na^+, c =

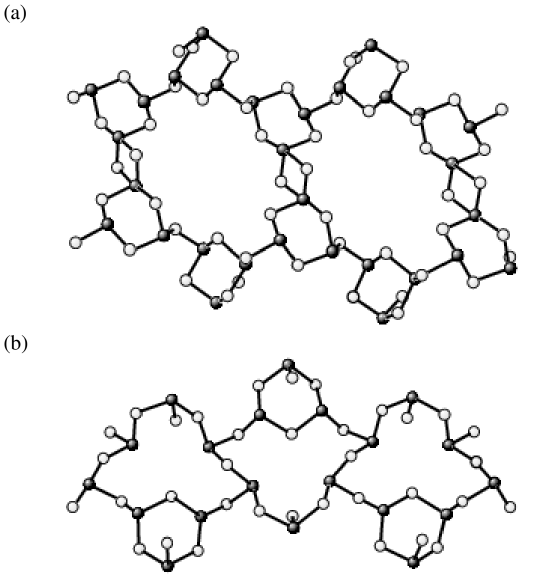


Fig. 3. Connectivity patterns in the $^1_\infty[\mathrm{As_6S_{10}}^{2-}]$ chains of (a) $(\mathrm{Me_4N})_2\mathrm{As_6S_{10}}$ [7] and (b) $(\mathrm{Et_4N})_2\mathrm{As_6S_{10}}$ [35].

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, $\mathrm{Cs_2As_8S_{13}}$ [37]. As illustrated in Fig. 4, the alkali metal cations induce the formation of eight-membered $\mathrm{As_4S_4}$ 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*-$[\mathrm{As_4}E_8]^{4-}$ anions have only been observed in $\mathrm{Cs_4As_4Se_8}$ [31], once again in the presence of Cs^+ counter cations. An interesting feature in both $\mathrm{Cs_2As_8S_{13}}$ 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 $(\mathrm{Me_4N})_2\mathrm{As_4S_7}$) to the other ring As atoms.

In striking contrast to the thioarsenate(III) system, hydrothermal reaction of alkali metal carbonates $A_2\mathrm{CO_3}$ (A = K, Rb, Cs) with $\mathrm{As_2Se_3}$ affords the compounds $\mathrm{KAsSe_3 \cdot H_2O}$ and $A\mathrm{AsSe_3 \cdot 0.5H_2O}$ (A = Rb, Cs), in which ψ-$\mathrm{AsSe_3}$ tetrahedra are linked through Se–Se bonds into $^1_\infty[\mathrm{AsSe^{3-}}]$ 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 $(\mathrm{Et_4N})\mathrm{Cl}$ with $\mathrm{As_2Se_3}$ and $\mathrm{Na_2Se}$ in acetonitrile at 110 °C (t = 11 d) affords $(\mathrm{Et_4N})[\mathrm{SeAs(Se_7}$-$\kappa^2\mathrm{Se}^1,\mathrm{Se}^7)]$ in good yield [35]. Somewhat surprisingly, the metaselenidoarsenates(III) $A\mathrm{AsSe_2}$ (A = K–Cs) with their $^1_\infty[\mathrm{AsSe_2}^-]$ chains can, however, can be prepared from $A_2\mathrm{CO_3}$ and $\mathrm{As_2Se_3}$ 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 $\mathrm{NaAsSe_2}$, by direct reaction of the elements at 700 °C [41b]. Whereas *zweier* repeat units are observed for $\mathrm{NaAsSe_2}$ and $\mathrm{CsAsSe_2}$, longer *vierer* units are found in both $\mathrm{KAsSe_2}$ and $\mathrm{RbAsSe_2}$ [40]. The failure of $\mathrm{AsSe_3}^{3-}$ anions to self-condense to polyselenidoarsenates(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 E^{2-} anions resulting from self-condensation reactions such as (2) will be less favorable for E = Se in comparison to E = S.

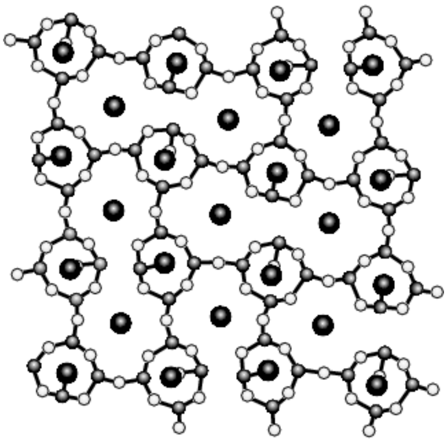


Fig. 4. The lamellar structure of the $^2_\infty[\mathrm{As_8S_{13}}^{2-}]$ anions in $\mathrm{Cs_2As_8S_{13}}$ [37].

The characteristic tendency of pyramidal $\mathrm{AsS_3}^{3-}$ anions to first condense through corner-bridging to $\mathrm{As_2S_5}^{4-}$ and *cyclo*-$[\mathrm{As_3S_6}]^{3-}$ anions and subsequently to 1D polymeric thioarsenate(III) anions under mild hydrothermal conditions in the presence of suitable counterions has already been discussed. This ability 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) AsS_3^{3-} – in α- and β-Ag_3AsS_3 [42],
$Tl_2SnAs_2S_6$ [43],
KCu_2AsS_3, KCu_4AsS_4 [44],
$K_2[Ag_6(AsS_3)(As_3S_7)]$ [32],
$K_2SnAs_2S_6$ [45], $TlHgAsS_3$ [46],
${}^{1}_{\infty}[\{Mn(tren)\}InAsS_4]$ [47]

(2) ${}^{1}_{\infty}[As_2S_4^{2-}]$ – in ${}^{1}_{\infty}[\{Mn(terpy)\}As_2S_4]$ [48]

(3) $As_2S_5^{4-}$ – in $Tl_2MnAs_2S_5$ [49],
$TlCuPbAs_2S_5$ [50], $TlAgPbAs_2S_5$ [51],
$(Me_4N)_2[(Mo_2O_2S_2)(\mu\text{-}As_2S_5)]$ [52],
${}^{2}_{\infty}[Mn_2(2,2'\text{-bpy})As_2S_5]$ [5],
$[\{Mn(phen)_2\}_2(\mu\text{-}As_2S_5)]$ [27],
$(Ph_4P)_4[\{Pd_3(As_3S_6)\}_2Pd(As_2S_5)_2]$ [53]

(4) *cyclo*-$[As_3S_6]^{3-}$
– in $(Me_4N)_2Rb[Bi(As_3S_6)_2]$ [54],
$(NH_4)[Ag_2As_3S_6]$ [55], $AgAsS_2$ [56]

(5) ${}^{1}_{\infty}[As_3S_6^{3-}]$ - in $(Me_4N)[Hg\{As_2S_4(AsS_2)\}]$ [57]

(6) *cyclo*-$[As_3S_5]^{3-}$ and $As_3S_6^{5-}$
– in $(Ph_4P)_2[Pt(As_3S_5)_2]$ [58] and
$(Ph_4P)_4[\{Pd_3(As_3S_6)\}_2Pd(As_2S_5)_2]$ [53],
respectively

(7) $[As_xS_{2x+1}]^{(x+2)-}$, $x = 3-5$
– in $(Ph_4P)_2[In(\mu\text{-}As_3S_7)]$ [54],
$K_2[Ag_6(AsS_3)(As_3S_7)]$ [32],
$(Ph_4P)_2[Hg_2As_4S_9]$ [57],
$[Cu_{12}(As_3S_7)(As_5S_{11})]$ [59]

(8) ${}^{1}_{\infty}[As_4S_7^{2-}]$ – in ${}^{1}_{\infty}[\{Mn(tren)\}As_4S_7]$ [48]

(9) $As_4S_8^{4-}$ – in $(Ph_4P)_2[Ni\{\mu\text{-}trans,$
$cyclo\text{-}As_2S_2(AsS_3)_2\}$ [52],
${}^{1}_{\infty}[\{Mn(terpy)\}_2\{\mu\text{-}cyclo\text{-}(As_4S_8)\}]$ [48]

(10) $As_6S_{12}^{6-}$ – in $Tl_2[Pb_2(As_6S_{12})]$ [60]

This list contains both open-chain anionic ligands of the type $[As_xS_{2x+1}]^{(x+2)-}$ ($As_2S_5^{4-}$, $As_3S_7^{5-}$, $As_4S_9^{6-}$, $As_5S_{11}^{7-}$ and ${}^{1}_{\infty}[As_2S_4^{2-}]$) and tri- and tetracyclic anions, *cyclo*-$[As_3S_6]^{3-}$ and *cyclo*-$[As_4S_8]^{4-}$, as simple corner-bridged self condensation products of pyramidal AsS_3^{3-} anions. In addition, a number of building units such as ${}^{1}_{\infty}[As_3S_6^{3-}]$, ${}^{1}_{\infty}[As_4S_7^{2-}]$, $[As_4S_8]^{4-}$, and $[As_6S_{12}]^{6-}$ with novel connectivity patterns have also been identified in ternary thioarsenate(III) anions.

With the exception of minerals such as Ag_3AsS_3 [42], $Tl_2SnAs_2S_6$ [43] and $[Cu_{12}(As_3S_7)(As_5S_{11})]$ [59], and the synthetic quaternary phase $K_2SnAs_2S_6$ [45], all of these compounds were prepared under mild solvothermal reaction conditions. $K_2SnAs_2S_6$ is isomorphic to $Tl_2SnAs_2S_6$ and contains ${}^{2}_{\infty}[SnAs_2S_6^{2-}]$ layers consisting of corner-sharing SnS_6 octahedra and AsS_3^{3-} pyramids. It was obtained in the polythioarsenate flux resulting from a mixture of K_2S, Sn, S and As_2S_3 in a silica tube at 500 ℃ [45]. The quaternary phases KCu_2AsS_3 and KCu_4AsS_4 were synthesized by solvothermal reaction of $KAsS_2$, Cu and S in supercritical ethylenediamine at respectively 300 and 350 ℃ [44]. A particularly interesting aspect of the ${}^{2}_{\infty}[Cu_2AsS_3^{-}]$ sheets of KCu_2AsS_3 is the tetrahedral coordination of half of their copper atoms by three sulfur atoms from different 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 Mn(II) atoms and as the solvothermal reaction medium for the generation of ${}^{1}_{\infty}[\{Mn(tren)\}InAsS_4]$ [47] from $MnCl_2$, $In(NO_3)_3$, As_2S_3 and S at $T = 160$ ℃. Pyramidal AsS_3^{3-} units share corners with dinuclear $In_2S_6^{6-}$ units to construct 1D chains (Fig. 5), whose charge is balanced by peripheral $[(tren)Mn]^{2+}$ fragments.

Both AsS_3^{3-} pyramids and linear $As_3S_7^{5-}$ chains participate in the ${}^{2}_{\infty}[Ag_3As_2S_5^{-}]$ layers of $KAg_3As_2S_5$, which was obtained by treating K_3AsS_3 with $AgBF_4$ at a 1 : 3 molar ratio in superheated methanol at T = 110 ℃ [32]. Kanatzidis *et al.* have employed

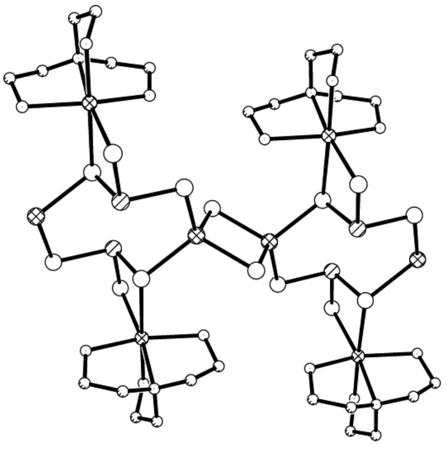


Fig. 5. A segment of the infinite chain structure of the quaternary thioarsenate(III) ${}^{1}_{\infty}[\{Mn(tren)\}InAsS_4]$ [47].

a general hydrothermal strategy involving treatment of a precursor $A\mathrm{AsS_3}$ (A = K, Rb) with the appropriate metal chloride ($\mathrm{BiCl_3}$, $\mathrm{HgCl_2}$, $\mathrm{PdCl_2}$, $\mathrm{InCl_3}$, $\mathrm{NiCl_2}$) or oxide ($\mathrm{MoO_3}$) in the presence of $(\mathrm{Me_4N})\mathrm{Cl}$ or $(\mathrm{Ph_4P})\mathrm{Br}$ in superheated water to afford the listed ternary tetramethylammonium and tetraphenylphosphonium thioarsenates(III) [52–54, 57]. The suitability of the protic aqueous medium for inducing self-condensation of $\mathrm{AsS_3}^{3-}$ 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 thioarsenates(III), but it is worth noting that Mn–S bonds to bridging S atoms are present in the infinite sheets of $[\mathrm{Mn_2(2,2'\text{-}bpy)As_2S_5}]$ (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 ${}^{2}_{\infty}[\{\mathrm{Bi(As_3S_6)_2}\}^{3-}]$ anions of the trigonal compound $(\mathrm{Me_4N})_2\mathrm{Rb}[\mathrm{BiAs_6S_{12}}]$ [54] is facilitated by the presence of a smaller Rb^+ cation (from the starting material $\mathrm{Rb_3AsS_3}$) in addition to two $\mathrm{Me_4N}^+$ counterions. The tridentate chair-shaped *cyclo*-$[\mathrm{As_3S_6}]^{3-}$ ligands exhibit crystallographic $C3$ 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 $\mathrm{K_2SnAs_2S_6}$ [45], whose denser ${}^{2}_{\infty}[\{\mathrm{Sn(AsS_3)_2}\}^{2-}]$ sheets contain simple tridentate $\mathrm{AsS_3}^{3-}$ pyramids rather than condensed trinuclear *cyclo*-$[\mathrm{As_3S_6}]^{3-}$- ligands.

Dinuclear corner-bridged $\mathrm{As_2S_5}^{4-}$ units have been found in a wide range of compounds including the minerals $\mathrm{Tl_2MnAs_2S_5}$ [49], $\mathrm{TlCuPbAs_2S_5}$ [50] and $\mathrm{TlAgPbAs_2S_5}$ [51]. The linear $\mathrm{As_3S_7}^{5-}$, $\mathrm{As_4S_9}^{6-}$ and $\mathrm{As_5S_{11}}^{7-}$ ligands of $(\mathrm{Ph_4P})_2[\mathrm{InAs_3S_7}]$ [54], $\mathrm{K_2[Ag_6(AsS_3)(As_3S_7)]}$ [32], $(\mathrm{Ph_4P})_2[\mathrm{Hg_2As_4S_9}]$ [57] and the mineral $[\mathrm{Cu_{12}(As_3S_7)(As_5S_{11})}]$ [59] are unknown as binary thioarsentate(III) anions, and this is also the case for the polymeric ${}^{1}_{\infty}[\mathrm{As_3S_6}^{3-}]$, ${}^{1}_{\infty}[\mathrm{As_4S_7}^{2-}]$ and *cyclo*-$[\mathrm{As_4S_8}]^{4-}$ anions of $(\mathrm{Me_4N})[\mathrm{Hg\{As_2S_4(AsS_2)\}}]$ [57], ${}^{1}_{\infty}[\{\mathrm{Mn(tren)}\}\mathrm{As_4S_7}]$ [48] and $[\{\mathrm{Mn(terpy)}\}_2\{\mu\text{-}(\mathrm{As_4S_8})\}]$ [48], respectively. The infinite ${}^{1}_{\infty}[\mathrm{As_3S_6}^{3-}]$ anions contain $\mathrm{As_2S_4}$ repeating units in which one of the arsenic atoms shares its terminal S atom with an additional pyramidal $\mathrm{AsS_3}^{3-}$ unit. In contrast to the polymeric thioarsenate(III) anions of the same formula type in $(\mathrm{Me_4N})_2\mathrm{As_4S_7}$ [7], the ${}^{1}_{\infty}[\mathrm{As_4S_7}^{2-}]$ anion of ${}^{1}_{\infty}[\{\mathrm{Mn(tren)}\}\mathrm{As_4S_7}]$ contains *cyclo*-$[\mathrm{As_4S_8}]^{4-}$ rather than *cyclo*-$[\mathrm{As_3S_6}]^{3-}$ building blocks. Connection of these eight-membered rings through corner-bridged dinuclear $\mathrm{As_2S_5}^{4-}$ units leads to the generation of the infinite double chains depicted in Fig. 6. Further condensation is prevented by the charge-balancing $\{\mathrm{Mn(tren)}\}^{2+}$ fragments that are attached to half of the terminal S atoms. ${}^{1}_{\infty}[\{\mathrm{Mn(tren)}\}\mathrm{As_4S_7}]$ was prepared by hydrothermal reaction of $[\mathrm{MnCl_2(tren)}]$ with $\mathrm{As_2S_3}$ at a 1 : 1 molar ratio at 160 °C in the presence of an equivalent of the mineralizer $\mathrm{Cs_2CO_3}$ [48].

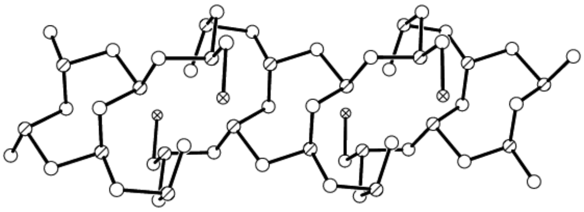


Fig. 6. A segment of the ${}^{1}_{\infty}[\mathrm{As_4S_7}^{2-}]$ chains of ${}^{1}_{\infty}[\{\mathrm{Mn(tren)}\}\mathrm{As_4S_7}]$ [48]. The tren ligands have been omitted for clarity.

The meridional coordination mode of the tridentate terpy ligand enables the pentacoordinated Mn(II) atoms of the $\{\mathrm{Mn(terpy)}\}^{2+}$ fragment to adopt a wide range of E–Mn–E' angles (96 – 121°) in its chalcogenidoarsenate(III) complexes. Treatment of $[\{\mathrm{Mn(terpy)}\}]$ with $\mathrm{As_2S_3}$ and $\mathrm{Cs_2CO_3}$ at an equimolar ratio in a superheated 10 : 1 $\mathrm{H_2O}$/en mixture leads to the formation of $[\{\mathrm{Mn(terpy)}\}_2(\mathrm{As_4S_8})]$ (Fig. 7) at 150 °C and to the coordination polymer ${}^{1}_{\infty}[\{\mathrm{Mn(terpy)}\}(\mathrm{As_2S_4})]$ (Fig. 8) at 190 °C [48]. The *cyclo*-$[\mathrm{As_4S_8}]^{4-}$ 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.

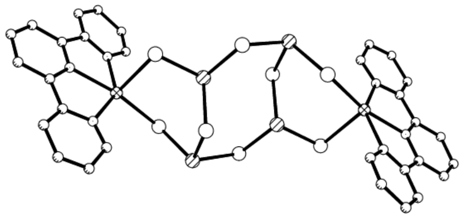


Fig. 7. Molecular structure of $[\{\mathrm{Mn(terpy)}\}_2(\mu\text{-}\mathrm{As_4S_8})]$ [48].

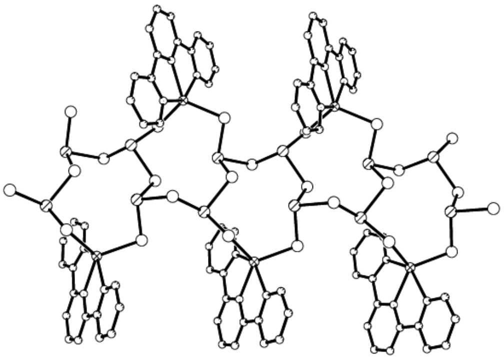


Fig. 8. A segment of the infinite chains of $^1_\infty$[{Mn(terpy)}-(As_2S_4)] [48].

It is interesting to note in this respect that the isomeric $As_4S_8^{4-}$ ligands of $(Ph_4P)_2[Ni(\mu\text{-}As_4S_8)]$ [52] contain a central corner-bridged *cyclo*-$[As_2S_4]^{2-}$ unit to which corner-sharing pyramidal AsS_3^{3-} units are attached in a *trans* arrangement. These $As_4S_8^{4-}$ ligands chelate Ni(II) atoms in the square-planar configuration and bridge to the next metal atom in an infinite $^1_\infty[\{Ni(\mu\text{-}As_4S_8\}^{2-}]$ chain. A central corner-bridged *cyclo*-$[As_2S_4]^{2-}$ unit is also present in the longer $As_6S_{12}^{6-}$ units of the mineral $Tl_2[Pb_2(As_6S_{12})]$ [60], but in this case the attached dinuclear $As_2S_5^{4-}$ units are sited *cis* to one another. The structure of the higher temperature phase $^1_\infty$[{Mn(terpy)}(As_2S_4)] is illustrated in Fig. 8. It can be regarded as containing $^1_\infty[AsS_2^-]$ chains that coordinate Mn(II) atoms through their terminal S atoms and incorporate these into ten-membered $MnAs_4S_5$ 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)° to the central imino nitrogen atom complementing the relatively wide S–Mn–S′ angle of 115.6(1)° within the $^1_\infty[MnAs_2S_4]$ double chain.

An unprecedented gondola-like structure has been established for the $[Pd_7As_{10}S_{22}]^{4-}$ anion of $(Ph_4P)_4[Pd_7As_{10}S_{22}]$, which was prepared by methanolothermal reaction of $PdCl_2$ with K_3AsS_3 and $(Ph_4P)Br$ at 110 °C for 3 days [53]. As may be seen in Fig. 9, two different thioarsenate ligands, $As_2S_5^{4-}$ and $As_3S_6^{5-}$, are linked to Pd(II) atoms in the square-planar configuration in this remarkable anion. The $As_3S_6^{5-}$ 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:

$$As_3S_7^{5-} + 2\,e^- \rightleftharpoons As_3S_6^{5-} + S^{2-} \qquad (4)$$

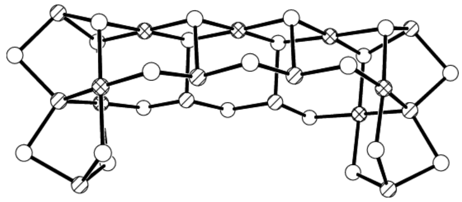


Fig. 9. The gondola-like structure of the $[\{Pd_3(As_3S_6)\}_2\text{-}Pd(As_2S_5)_2]^{4-}$ anion of $(Ph_4P)_4[Pd_7As_{10}S_{22}]$ [53] with its $As_3S_6^{5-}$ and $As_2S_5^{4-}$ ligands.

AsS_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_3AsS_3 and $(Ph_4P)Br$ at 110 °C [58]. Oxidation of Pt(II) atoms to Pt(IV) provides the electrons for the reduction in this case. Each of the resulting *cyclo*-$[As_3S_5]^{3-}$ anions in the product $(Ph_4P)_2[Pt(As_3S_5)_2]$ 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) $^1_\infty[AsSe_2^-]$
– in $K_2AgAs_3Se_6$, $Rb_2AgAs_3Se_6$ [61],
$CsAgAs_2Se_4$, $Cs_3AgAs_4Se_8$ [62],
$^1_\infty$[{Mn(tren)}As_2Se_4] [12]

(2) $AsSe_3^{3-}$
– in α- und β-Ag_3AsSe_3 [63,32],
$Cs_3AsGeSe_5$ [14]
$Cs_4[Bi(AsSe_3)\{trans\text{-}(As_2Se_4)\}]$ [15],
$(Me_4N)[HgAsSe_3]$, $(Et_4N)[HgAsSe_3]$ [64],
$A_3[M_2Se_2(Se_2)_3(AsSe_3)]$,
(A = K, Rb, Cs; M = Nb, Ta [65])

(3) $As_2Se_5^{4-}$
– in $K_3AgAs_2Se_5 \cdot 0.25\,CH_3OH$ [61],
$(Me_3NH)[Ag_3As_2Se_5]$ [32],
$(Et_4N)_2[(Mo_2O_2Se_2)(\mu\text{-}As_2Se_5)]$ [52],
$[\{Mn(tren)\}_2(\mu\text{-}As_2Se_5)]$ [6],
$[\{Mn(terpy)\}_2(\mu\text{-}As_2Se_5)]_2$ [48]

(4) *cyclo*-$[As_3Se_6]^{3-}$ – in $RbAg_2As_3Se_6$ [66]

(5) $^1_\infty[As_4Se_7^{2-}]$ – in $^1_\infty$[{Mn(tren)}As_4Se_7] [12]

(6) *cyclo*-$[As_4Se_8]^{4-}$
– in [{Mn(terpy)}$_2${μ-*cyclo*-(As_4Se_8)}] [48]

With the exception of α-Ag_3AsSe_3, which was synthesized from a high-temperature flux of the elements 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 $K_2AgAs_3Se_6$, $Rb_2AgAs_3Se_6$, $K_3AgAs_2Se_5 \cdot 0.25\ CH_3OH$ [61], $Cs_3AgAs_4Se_8$, and $CsAgAg_2Se_4$ were all prepared by methanolothermal reaction of $AsSe_3{}^{3-}$ anions (sources Li_3AsSe_3 or K_3AsSe_3) with $AgBF_4$ 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 Cs_2CO_3) were also employed to synthesize $Cs_3AsGeSe_5$, which represents the first example of a mixed Ge(IV)/As(III) chalcogenidometalate and contains *zweier* $^1_\infty[AsGeSe_5{}^{3-}]$ chains in which alternating $AsSe_3{}^{3-}$ pyramids and $GeSe_4{}^{4-}$ tetrahedra share common corners [14]. $(Et_4N)_2[(Mo_2O_2Se_2)(\mu\text{-}As_2Se_5)]$ was obtained under hydrothermal conditions by treating MoO_3 with K_3AsSe_3 and $(Et_4N)Br$ 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 $As_2Se_5{}^{4-}$ anion and the ring-shaped anions *cyclo*-$[As_xSe_{2x}]^{x-}$, x = 3, 4. Although infinite $^1_\infty[AsSe_2{}^-]$ chains have been found in five different compounds, no examples for linear ligands $[As_xSe_{2x+1}]^{(x+2)-}$ (x = 3 – 5) appear to be known. Several of the compounds have thioarsenate(III) analogs, for instance $(Et_4N)_2[(Mo_2O_2Se_2)(\mu\text{-}As_2Se_5)]$ [52], $^1_\infty[\{Mn(tren)\}As_4Se_7]$ [12] and $[\{Mn(terpy)\}_2As_4Se_8]$ [48]. In the molybdenum(V) complexes, $[Mo_2O_2E_2]^{2+}$ cores (E = S, Se) are linked by corner-bridged dinuclear $As_2E_5{}^{4-}$ ligands which chelate neighboring metal atoms through their terminal chalcogen atoms. The manganese(II) complexes $^1_\infty[\{Mn(tren)\}As_4Se_7]$ and $[\{Mn(terpy)\}_2As_4Se_8]$ were obtained under hydrothermal conditions at 150 °C by treating respectively $[MnCl_2(tren)]$ or $[MnCl_2(terpy)]$ with elemental As and Se at molar ratios of 1 : 6 : 12 or 1 : 4 : 8 in the presence of the mineralizer Cs_2CO_3. Whereas isolated *cyclo*-$[As_4Se_8]^{4-}$ anions have been structurally characterized in $Cs_4As_4Se_8$ [31], the $^1_\infty[As_4Se_7{}^{2-}]$ chains of $^1_\infty[\{Mn(tren)\}As_4Se_7]$ (see Fig. 6 for the thioarsenate(III) analog) are unknown for binary selenidoarsenate(III) anions. Indeed, these 1D polymeric anions represent the only known example for a selenidoarsenate(III) anion with a condensation grade c (= 0.571) greater than that of 0.50 found in $^1_\infty[AsSe_2{}^-]$ and *cyclo*-$[As_xSe_{2x}]^{x-}$, x = 3, 4.

The connectivity pattern of the Mn, As and Se atoms in $^1_\infty[\{Mn(tren)\}As_2Se_4]$ [12] is closely related to that of the Mn, As and S atoms in $^1_\infty[\{Mn(terpy)\}As_2S_4]$ (Fig. 8). As the $\{Mn(tren)\}^{2+}$ 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 $^1_\infty[MnAs_2S_4]$ chains of $^1_\infty[\{Mn(terpy)\}\ As_2S_4]$ 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].

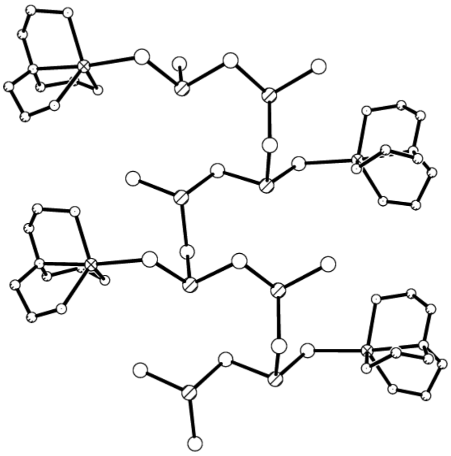


Fig. 10. A segment of the infinite *vierer* chains of $^1_\infty[\{Mn(tren)\}As_2Se_4]$ [12].

Chalcogenidoarsenates(III) Containing Oligochalcogenide Ligands $E_n{}^{2-}$ (n = 2 – 7)

Alkali metal oligochalcogenides are well-known to dissociate into chain anions $E_n{}^{2-}$ 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 $E_{n-x}{}^{2-}$ 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 $E_n{}^{2-}$ 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 $AsE_3{}^{3-}$ anions to self-condense in the order S > Se ≫ Te.

Table 3. Compounds containing discrete thio- or selenidoarsenate(III) anions with oligochalcogenide ligands E_n^{2-} (n = 2, 3, 5, 7).

Anion	E = S	E = Se
$^1_\infty[\mathrm{As}E_3{}^-]$		$\mathrm{KAsSe_3 \cdot H_2O}$ [39] $A\mathrm{AsSe_3 \cdot 0.5\,H_2O}$ (A = Rb, Cs) [39]
$[E\mathrm{As}(E_5\text{-}\kappa^2E^1,E^5)]^-$	$\mathrm{(Ph_4P)[SAsS_5]}$ [67]	$\mathrm{(enH)[SeAsSe_5] \cdot}$ 2.2.2-crypt [68] $\mathrm{(Ph_4P)[SeAsSe_5]}$ [69]
$[E\mathrm{As}(E_7\text{-}\kappa^2E^1,E^7)]^-$	$\mathrm{(Ph_4P)[SAsS_7]}$ [70]	$\mathrm{(Et_4N)[SeAsSe_7]}$ [68]
$[(E\mathrm{As})_2(\mu\text{-}E)(\mu\text{-}E_3)]^{2-}$	$\mathrm{(Ph_4P)_2[As_2S_6]}$ [71]	
$[(E\mathrm{As})_2(\mu\text{-}E_2)_2]^{2-}$		$\mathrm{[Na(2.2.2\text{-}crypt]_2[As_2Se_6]}$ [72] $\mathrm{(Ph_4P)_2As_2Se_6}$ [73] refs. [30, 68, 69, 74, 75][a]

[a] Ref. [30]: $[M\mathrm{(en)_3]As_2Se_6}$, M = Mn, Fe; ref. [68]: $\mathrm{(Et_4N)_2As_2Se_6}$; ref. [69]: $\mathrm{(Ph_4P)_2\text{-}As_2Se_6 \cdot 2CH_3CN}$; ref. [74]: $\mathrm{[Cs(18\text{-}crown\text{-}6)]_2\text{-}(As_2Se_6)}$; ref. [75]: $\mathrm{[Mn(9\text{-}aneN_3)_2]As_2Se_6}$.

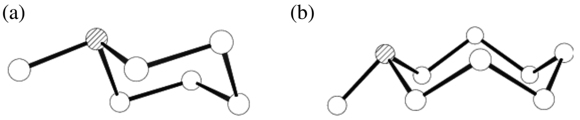


Fig. 11. The *cyclo*-$[\mathrm{SeAsSe_5}]^-$ and *cyclo*-$[\mathrm{SeAsSe_7}]^-$ anions of (a) $\mathrm{(Ph_4P)[SeAsSe_5]}$ [69] and (b) $\mathrm{(Et_4N)[SeAsSe_7]}$ [68], respectively.

Table 3 lists the known binary thio- and selenidoarsenate(III) anions containing oligochalcogenide ligands E_n^{2-} (n = 2, 3, 5, 7). The cyclic anions $[E\mathrm{As}E_5]^-$, $[E\mathrm{As}E_7]^-$ (E = S, Se) and $[\mathrm{As_2S_6}]^{2-}$ were all extracted from low-temperature ($T \leq 60$ °C) chalcogen-rich reaction solutions by employing bulky counterions ($\mathrm{Ph_4P^+}$, $\mathrm{Et_4N^+}$, $\mathrm{enH^+}$). For instance, $\mathrm{(Ph_4P)[SAsS_7]}$ was obtained by reaction of $\mathrm{(Ph_4P)[As_2SCl_5]}$ with $\mathrm{K_2S_5}$ in acetonitrile at r. t. [70] and $\mathrm{(Et_4N)[SeAsSe_7]}$ by heating an alloy of nominal composition ”$\mathrm{AsSe_4}$” to 60 °C in ethylenediamine for 8 h and then layering the resulting dark red solution at r. t. with en saturated with $\mathrm{(Et_4N)Br}$ [68]. The respectively chair- and crown-shaped rings of the $[\mathrm{SeAsSe_5}]^-$ and $[\mathrm{SeAsSe_7}]^-$ anions are depicted in Fig. 11 and can be regarded as representing substitution products of the similarly shaped allotropes of selenium, *cyclo*-$\mathrm{Se_6}$ and *cyclo*-$\mathrm{Se_8}$.

The chair-shaped *cyclo*-$[\mathrm{As_2Se_6}]^{2-}$ anion (Fig. 12b) has been obtained both at r. t. and under mild solvothermal conditions (examples for the latter synthetic approach are given for $A = [M\mathrm{(en)_3}]$, M = Mn, Fe [30]; $A = [\mathrm{Mn(9\text{-}ane\text{-}N_3)_2}]$ [75]) and has been stabilized in the presence of a wide range of counterions. It is isomeric with the infinite $^1_\infty[\mathrm{AsSe^{3-}}]$ chains of $\mathrm{KAsSe_3 \cdot H_2O}$ and $A\mathrm{AsSe_3 \cdot 0.5H_2O}$ (A = Rb, Cs), which were obtained by hydrothermal reaction of $\mathrm{As_2Se_3}$ with the appropriate alkali metal carbonate at 135 °C [39]. Although entropy considerations might suggest that condensation of $\mathrm{AsSe_3}^{3-}$ anions to corner-bridged species such as *cyclo*-$[\mathrm{As_3Se_6}]^{3-}$ or $^1_\infty[\mathrm{AsSe_2}^-]$ 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 $\mathrm{As_2Te_6}^{2-}$ anion has also been structurally characterized in $\mathrm{(Ph_4P)_2As_2Te_6}$ [76] and $\mathrm{[K(2.2.2\text{-}crypt)]_2As_2Te_6}$ [77] but that both the analogous $[\mathrm{(SAs)_2(\mu\text{-}S_2)_2}]^{2-}$ and $^1_\infty[\mathrm{AsS_3}^-]$ anions are unknown. However, the isomeric chair-shaped $[\mathrm{(SAs)_2(\mu\text{-}S)(\mu\text{-}S_3)}]^{2-}$ anion (Fig. 12a) has been characterized in the compound $\mathrm{(Ph_4P)_2As_2S_6}$, which was obtained by treating $\mathrm{Na_3AsS_4}$ with $\mathrm{(Ph_4P)Cl}$ in DMF at r. t. [71]. Whereas the endocyclic bond angles in the $\mathrm{As_2S_6}^{2-}$ anion of $\mathrm{(Ph_4P)_2As_2S_6}$ 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 $\mathrm{[Na(2.2.2\text{-}crypt)]_2As_2Se_6}$ [72]) is observed for the ring angles within the $\mathrm{As_2Se_6}^{2-}$ anion. In addition, as also found in the $^1_\infty[\mathrm{AsSe^{3-}}]$ chains of $\mathrm{KAsSe_3 \cdot H_2O}$ and $A\mathrm{AsSe_3 \cdot 0.5\ H_2O}$ (A = Rb, Cs) [39], rather narrow exocyclic Se_t–As–Se_b angles (t = terminal, b = bridging) are present in the latter anion (*e. g.* 95.1(1) and 96.5(1)° in $\mathrm{[Na(2.2.2\text{-}crypt)]_2As_2Se_6}$ [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 S_t–As–S_b angles between 99.8(1) and 101.6(1)° are found in the $\mathrm{As_2S_6}^{2-}$ anion of $\mathrm{(Ph_4P)_2As_2S_6}$ [71]. This molecular geometry analysis suggests that the cyclic $\mathrm{As_2Se_6}^{2-}$ anions may represent an energetically favorable connectivity pattern.

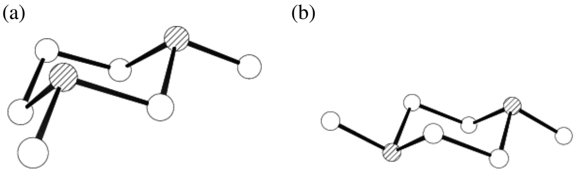


Fig. 12. The *cyclo*-$[\mathrm{As_2S_6}]^{2-}$ and *cyclo*-$[\mathrm{As_2Se_6}]^{2-}$ anions of (a) $\mathrm{(Ph_4P)_2[As_2S_6]}$ [71] and (b) $\mathrm{(Ph_4P)_2[As_2Se_6]}$ [73], respectively.

Although discrete anions of the types $[\mathrm{As}E_2(E_2)]^{3-}$ and $[\mathrm{As}E(E_2)_2]^{3-}$ are unknown, such mononu-

Table 4. Compounds containing thio- or selenidoarsenate(III) ligands with E_n^{2-} units (n = 2, 3).

Ligand	E = S	E = Se
$[\mathrm{As}E_2(E)]^{3-}$	$\mathrm{Cs_2[Sn(AsS_4)(AsS_5)]}$ [78] $\mathrm{K[SnS(AsS_4)]}$ [45] $\mathrm{[(C_5Me_4Et)_3Co_3S(AsS_4)]I}$ [79] $\mathrm{(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5H_2O}$ [58]	$\mathrm{Cs_2[Sn(AsSe_4)(AsSe_5)]}$ [78] $\mathrm{[In(en)_2(AsSe_4)]\cdot en}$ [68] $\mathrm{[(C_5Me_4Et)_3Co_3Se(AsSe_4)]I}$ [79] $(n\text{-}\mathrm{Bu_4N})_4\mathrm{[Cu_7Se(AsSe_4)_3]}$ [80] $\mathrm{[\{Mn(terpy)\}_3(AsSe_4)_2]}$ [81]
$[\mathrm{As}E(E_2)_2]^{3-}$	$\mathrm{Cs_2[Sn(AsS_4)(AsS_5)]}$ [78] $\mathrm{[(C_5Me_4Et)_3Co_3S(AsS_5)]I}$ [79]	$\mathrm{Cs_2[Sn(AsSe_4)(AsSe_5)]}$ [78] $(n\text{-}\mathrm{Bu_4N})_2[M\mathrm{(AsSe_5)_2}]$ M = Mo, W [82, 83] $\mathrm{(Ph_4P)_2[W_2Se_3(AsSe_5)_2]}$ [82]
$[\mathrm{As_2}E_6]^{2-}$		$[\mathrm{\{Mn(tren)\}_2}(\mu\text{-}\mathrm{As_2Se_6})_2]$ [6]
$[\mathrm{As_2}E_6]^{4-}$		$[\mathrm{\{Mn(cyclam)\}_2}(\mu\text{-}\mathrm{As_2Se_6})]$ [81]
$[\mathrm{As_4}E_{11}]^{6-}$		$\mathrm{(Ph_4P)_2[Hg_2As_4Se_{11}]}$ [64]
$[\mathrm{As_4}E_{12}]^{4-}$	$\mathrm{(Ph_4P)_2[Mo_2O_2S_2}(\mu\text{-}\mathrm{As_4S_{12}})]$ [84]	

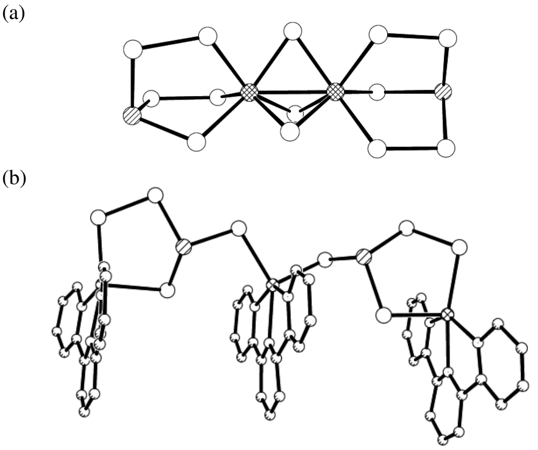


Fig. 13. $[\mathrm{AsSe_2(Se_2)}]^{3-}$ and $[\mathrm{AsSe(Se_2)_2}]^{3-}$ ligands in (a) $\mathrm{(Ph_4P)_2[W_2Se_3(AsSe_5)_2]}$ [82] and (b) $[\mathrm{\{Mn(terpy)\}_3(AsSe_4)_2}]$ [81], respectively.

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 $\mathrm{Cs_2SnAs_2}E_9$ [78] and $\mathrm{KSnAsS_5}$ [45]), extraction from appropriate alloys with ethylenediamine (for $(n\text{-}\mathrm{Bu_4N})_4\mathrm{[Cu_7As_3Se_{13}]}$ [80] and $\mathrm{[In(en)_2(AsSe_4)]\cdot en}$ [68]) and room-temperature reactions of $M\mathrm{Se_4}^{2-}$ anions (M = Mo, W) with $\mathrm{As_4Se_4}$ in DMF (for $(n\text{-}\mathrm{Bu_4N})_2\mathrm{[MAs_2Se_{10}]}$ and $\mathrm{(Ph_4P)_2[W_2As_2Se_{13}]}$ [82, 83]). $\mathrm{[(C_5Me_4Et)_3Co_3AsS_5]I}$ was prepared together with $\mathrm{[(C_5Me_4Et)_3Co_3AsS_6]I}$ and $\mathrm{[(C_5Me_4Et)_3Co_2As_2S_3]}$ by reaction of $\mathrm{K_3AsS_3}$ with $\mathrm{[(C_5Me_4Et)_3Co_2(CO)I_2]}$ in DMF at 120 °C [79]. Treatment of $\mathrm{[(C_5Me_4Et)_3Co_2I_4]}$ with $\mathrm{K_2As_4Se_6}$ in DMF at the same temperature affords $\mathrm{[(C_5Me_4Et)_3Co_3AsSe_5]I}$ [79]. 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 $[\mathrm{As}E_2(E_2)]^{3-}$ and $[\mathrm{As}E(E_2)_2]^{3-}$ 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 $\mathrm{AsSe_5}^{3-}$ ligands adopt an energetically favorable tripodal $\kappa^3\mathrm{Se}^1,\mathrm{Se}^4,\mathrm{Se}^5$ coordination mode in the compound $\mathrm{(Ph_4P)_2[W_2Se_3(AsSe_5)_2]}$ [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 $\mathrm{As}E_4^{3-}$ and $\mathrm{As}E_5^{3-}$ anions more electron donating than $\mathrm{As}E_3^{3-}$ pyramids, which should be preferred by metal atoms in higher oxidation states such as the Sn(IV) atoms in $\mathrm{Cs_2SnAs_2}E_9$ and the W(V) atoms in $\mathrm{(Ph_4P)_2[W_2Se_3(AsSe_5)_2]}$.

$\mathrm{As}E_4^{3-}$ and $\mathrm{As}E_5^{3-}$ ligands have also been obtained under mild solvothermal conditions. For instance, $\mathrm{(Ph_4P)_2K[Pt_3(AsS_4)_3]\cdot 1.5H_2O}$ was prepared by hydrothermal reaction of $\mathrm{K_3AsS_3}$ with $\mathrm{(Ph_4P)Br}$ and $\mathrm{PtCl_2}$ at 110 °C and contains a trinuclear anion with a central chair-shaped $\mathrm{Pt_3S_3}$ ring and three tetradentate $\mathrm{AsS_4}^{3-}$ ligands that chelate adjacent Pt atoms in a $\mu_2\text{-}1\kappa^2\mathrm{S}^1\mathrm{S}^4 : 2\kappa^2\mathrm{S}^2,\mathrm{S}^4$ mode and also bridge these through the terminal bidentate S^4 atoms of their $\mathrm{S_2}$ units [58]. A contrasting $\mu_2\text{-}1\kappa^2\mathrm{Se}^1,\mathrm{Se}^4 : 2\kappa\mathrm{Se}^2$ tridentate bridging mode is adopted by the $\mathrm{AsSe_4}^{3-}$ ligands in the linear trinuclear complex $[\mathrm{\{Mn(terpy)\}_3}(\mu\text{-}\mathrm{AsSe_4})_2]$, whose structure is depicted in Fig. 13b. This compound was prepared by hydrothermal reaction (T = 150 °C) of $\mathrm{[MnCl_2(terpy)]}$ with elemental As and Se at a 1 : 1 : 2 molar ratio in the presence of

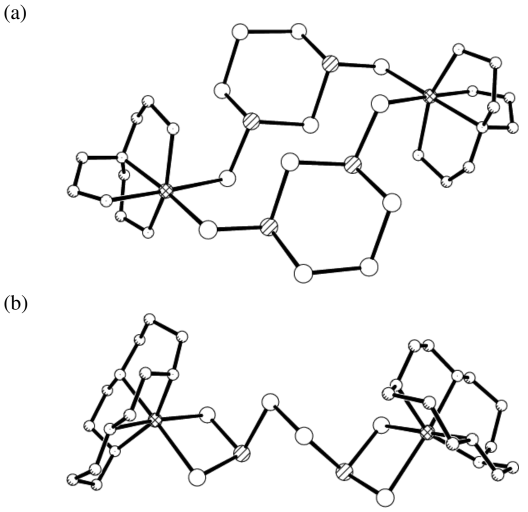


Fig. 14. Bridging $As_2Se_6{}^{z-}$ ligands (z = 2, 4) in (a) $[\{Mn(tren)\}_2(\mu\text{-}As_2Se_6)_2]$ [6] and (b) $[\{Mn(cyclam)\}_2(\mu\text{-}As_2Se_6)]$ [6], respectively.

Cs_2CO_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 $[\{Mn(terpy)\}_2(\mu\text{-}As_2Se_4)]\cdot 2H_2O$ [6], which contains a bridging tetradentate $As_2Se_4{}^{4-}$ ligand with a central As–As bond. The nature of chalcogenidodiarsenate(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_2O/tren (10 : 1) at T = 150 °C affords $[\{Mn(tren)\}_2(\mu\text{-}As_2Se_5)]$ with bridging dipyramidal $As_2Se_5{}^{4-}$ 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_2O/CH_3OH (1 : 1) yields $[\{Mn(cyclam)\}_2(\mu\text{-}As_2Se_6)]$ (Fig. 14b) with a novel bridging $[(AsSe_2)_2(\mu\text{-}Se_2)]^{4-}$ ligand [81]. Increasing the $[MnCl_2(tren)]$: As : Se ratio to 1 : 3 : 5 and 1 : 6 : 12 leads to formation of $[\{Mn(tren)\}_2(\mu\text{-}As_2Se_6)_2]$ (Fig. 14a) [6] and polymeric $^{1}_{\infty}[\{Mn(tren)\}(As_4Se_7)]$ [12], respectively. In contrast to the adaptability of the $\{Mn(tren)\}^{2+}$ fragment towards chelating ligands or ligand pairs with a wide range of Se–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)° in $[\{Mn(cyclam)\}_2(\mu\text{-}As_2Se_6)]$). A relatively wide Se–Mn–Se′ angle of 97.31(6)° is observed in $[\{Mn(tren)\}_2(\mu\text{-}As_2Se_6)_2]$, whose cyclic $As_2Se_6{}^{2-}$ dianions can be regarded as being derived from the $As_2Se_5{}^{4-}$ tetraanion of $[\{Mn(tren)\}_2(\mu\text{-}As_2Se_5)]$ by addition of the central Se atom of the Se_3 unit. Although discrete $As_2Se_6{}^{2-}$ anions of this type appear to be unknown, the analogous $As_2S_6{}^{2-}$ anion has been characterized in $(Ph_4P)_2As_2S_6$ (Fig. 12a, [71]).

Two tetranuclear chalcogenidoarsenate(III) anions with $E_n{}^{2-}$ units have been described in the literature. The corner-bridged linear $As_4Se_{11}{}^{6-}$ ligands of the hydrothermal phase $(Ph_4P)_2[Hg_2As_4Se_{11}]$ [64] contain terminal dumb-bell Se_2 units at their first and fourth As atoms and are closely related to the $As_4S_9{}^{6-}$ ligands of the analogous thioarsenate(III) $(Ph_4P)_2[Hg_2As_4S_9]$ [57]. In contrast, the bridging $As_4S_{12}{}^{4-}$ ligands of $(Ph_4P)_2[Mo_2O_2S_2(\mu\text{-}As_4S_{12})]$, which is the product of the reaction of $(Ph_4P)_2MoS_4$ with realgar As_4S_4 in acetonitrile at r. t. [84] followed by DMF extraction, exhibit a central eight-membered $(AsS_3)_2$ ring, whose As atoms are corner-bridged to AsS_3 pyramids. The terminal S atoms of these AsS_3 units coordinate the Mo atoms in four-membered chelate rings.

Whereas $[AsTe_2(Te_2)]^{3-}$ ligands are known in $(n\text{-}Bu_4N)_2[\{Fe(CO)_2\}_2(\mu\text{-}AsTe_4)_2]$ [76], $(n\text{-}Bu_4N)_4[Cu_7Te(AsTe_4)_3]$ [85] and the analogous silver cluster anion of $(n\text{-}Bu_4N)_4[Ag_7Te(AsTe_4)_3]$ [80], no examples of coordinating $[AsTe(Te_2)_2]^{3-}$ species have been reported.

Lower Oxidation State Chalcogenidoarsenates

Chalcogenidoarsenate anions $As_xE_y{}^{z-}$ with direct As–As bonds can be classified as either chalcogen-rich ($y \geq x$) or chalcogen-poor ($y < x$). Examples for the former type of anion are provided by the bicyclic anions $As_4E_6{}^{2-}$ (E = S, Se), the polymeric selenidoarsenate(II,III) anions $^{1}_{\infty}[As_4Se_6{}^{2-}]$ and $^{1}_{\infty}[As_5Se_9{}^{5-}]$ and the telluridoarsenate(II) anions $As_2Te_4{}^{4-}$, $^{1}_{\infty}[As_2Te_5{}^{2-}]$, $As_2Te_6{}^{4-}$, and *cyclo*-$[As_4Te_6]^{4-}$ (Table 5). It is apparent from this list that the lower oxidation state II is more favorable for telluridoarsenates in comparison to S- and Se-containing anions. In contrast, as discussed in Sections 2 and 3, the *cyclo*-$As_2Te_6{}^{2-}$ anion provides the only example of a telluridoarsenate with As in its typical oxidation state III. The stability of the telluridoarsenates(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.

Anion	Examples
$\mathrm{As_2Te_4}^{4-}$	$A_4\mathrm{As_2Te_4}$, A = Na [89], K [90] $\mathrm{Rb_4As_2Te_4 \cdot en}$ [91]
$^{1}_{\infty}[\mathrm{As_2Te_5}^{2-}]$	$\mathrm{(Et_4N)_2As_2Te_5}$ [92]
$\mathrm{As_2Te_6}^{4-}$	$\mathrm{Cs_4As_2Te_6}$ [93]
cyclo-$[\mathrm{As_4Te_6}]^{4-}$	$\mathrm{(Me_4N)_4As_4Te_6 \cdot 2en}$ [93] $\mathrm{[Ba(en)_4]_2As_4Te_6}$ [94]

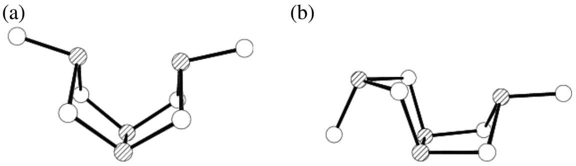


Fig. 15. The contrasting *endo-endo* and *exo-endo* conformations for the $[\mathrm{As_4}E_6]^{2-}$ anions in (a) $\mathrm{(pipH)_2[As_4S_6]}$ [86] and (b) $\mathrm{[K(2.2.2\text{-}crypt)]_2[As_4Se_6]}$ [23], respectively.

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

The $\mathrm{As_4S_6}^{2-}$ anion has been characterized in $\mathrm{(pipH)_2As_4S_6}$ (pip = piperidine) [86], $\mathrm{3Rb_2As_4S_6 \cdot As_4S_3}$ [34], $\mathrm{(Ph_4P)_2As_4S_6}$ [87] and $(n\text{-}\mathrm{Pr_2NH_2})_2\mathrm{As_4S_6}$ [88] and exhibits the *endo-endo* conformation (Fig. 15a) in all of these compounds. Whereas an *endo-endo* arrangement has also been established for the analogous $\mathrm{As_4Se_6}^{2-}$ anion in $\mathrm{(Ph_4P)_2As_4Se_6}$ [73], the alternative *endo-exo* variant (Fig. 15b) has been found in $\mathrm{[K(2.2.2\text{-}crypt)]_2As_4Se_6}$ [23]. Both of these $\mathrm{As_4Se_6}^{2-}$ anions can be prepared by reducing $\mathrm{As_4Se_4}$ with potassium, in the former case in DMF in the presence of $\mathrm{(Ph_4P)Br}$ and in the latter case in liquid ammonia in a flask containing the sequestering agent 2.2.2-crypt. Cleavage of one of the As–As bonds in the $\mathrm{As_4Se_4}$ cage by nucleophilic attack through two Se^{2-} anions will lead to the basket-like anion depicted in Fig. 15b with its two exocyclic As–Se bonds. It is interesting to note that the $\mathrm{As_4Se_6}^{2-}$ anion can be detected by ^{77}Se NMR spectroscopy immediately after $\mathrm{As_4Se_4}$ is dissolved in ethylenediamine, and that $\mathrm{(Ph_4P)_2As_4Se_6}$ can be isolated from the resulting solution following addition of $\mathrm{(Ph_4P)Br}$ [73]. Preparation of $\mathrm{(pipH)_2As_4S_6}$ was achieved in a similar manner by treatment of a solution of realgar in $\mathrm{CH_3NH(CH_2)_2OH}$ with piperidine [86]. In contrast to $\mathrm{As_4Se_6}^{2-}$, compounds containing $\mathrm{As_4S_6}^{2-}$ anions have also been obtained under mild solvothermal reducing conditions. For instance, $\mathrm{3Rb_2As_4S_6 \cdot As_4S_3}$ was prepared by hydrothermal reaction of $\mathrm{As_2S_3}$ with $\mathrm{Rb_2CO_3}$ at 130 °C [34], and $(n\text{-}\mathrm{Pr_2NH_2})_2\mathrm{As_4S_6}$ 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 $[n\text{-}\mathrm{Pr_2NH_2}]^+$ cations [88]. Salts of the *cyclo*-$[\mathrm{As_2Se_6}]^{2-}$ anion have often been isolated under similar solvothermal conditions when suitable large mono- or dications were available. This suggests that the bicyclic $\mathrm{As_4S_6}^{2-}$ species may represent a thioarsenate counterpart to $\mathrm{As_2Se_6}^{2-}$ 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 $\mathrm{As_2Se_3}$ with $A_2\mathrm{CO_3}$ (A = K, Rb, Cs) leads to the formation of polymeric anions $^{1}_{\infty}[\mathrm{AsSe_3}^-]$ in which μ-$\mathrm{AsSe_3}$ tetrahedra are linked by Se–Se bonds [39]. In contrast, metaselenidoarsenate(III) chains $^{1}_{\infty}[\mathrm{AsSe_2}^-]$ 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 $^{1}_{\infty}[\mathrm{AsSe_3}^-]$ chains or their possible fragment ions *cyclo*-$[\mathrm{As_2Se_6}]^{2-}$ in superheated methanol. Would the selenium-rich $^{1}_{\infty}[\mathrm{AsSe_3}^-]$ anions disproportionate to highly condensed selenidoarsenate(III) and polyselenido $\mathrm{Se}_n{}^{2-}$ anions or alternatively to mixed oxidation state selenidoarsenate(II,III) and $\mathrm{Se}_n{}^{2-}$ anions? In fact, heating $\mathrm{CsAsSe_3 \cdot 0.5H_2O}$ to 190 °C in methanol leads to the formation of the black selenidoarsenate(II,III) $\mathrm{Cs_2As_4Se_6}$ [16] and $\mathrm{Cs_2Se_5}$ as major products, together with deep-red $\mathrm{Cs_5As_5Se_9}$ and red $\mathrm{Cs_4As_4Se_8}$ [31] with its *cyclo*-$[\mathrm{As_4Se_8}]^{4-}$ anions (Fig. 1b) as accompanying minor products. A plausible stoichiometric equation (5) for the predominant disproportionation reaction can be formulated as follows:

$$4\,\mathrm{CsAsSe_3} \rightleftharpoons \mathrm{Cs_2As_4Se_6} + \mathrm{Cs_2Se_5} + \mathrm{Se} \tag{5}$$

As depicted in Fig. 16a, the selenidoarsenate(II,III) chains of $\mathrm{Cs_2As_4Se_6}$ contain dipyramidal $\mathrm{As_2Se_4}^{4-}$ building units that share Se atoms with $\mathrm{AsSe_3}^{3-}$ pyramids in five-membered $\mathrm{As_3Se_5}$ rings and are bridged at the same time by other $\mathrm{AsSe_3}^{3-}$ 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), $\mathrm{Cs_5As_5Se_9}$, was also present in the mixture of reaction products. The novel infinite $^{1}_{\infty}[\mathrm{As_5Se_9}^{5-}]$ chains of this phase are presented for the first time in this article

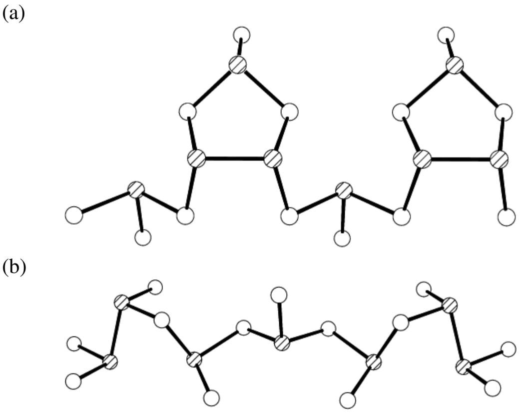


Fig. 16. The 1D ${}^{1}_{\infty}[As_4Se_6{}^{2-}]$ and ${}^{1}_{\infty}[As_5Se_9{}^{5-}]$ anions in (a) $Cs_2As_4Se_6$ [16] and (b) $Cs_5As_5Se_9$ (this work), respectively.

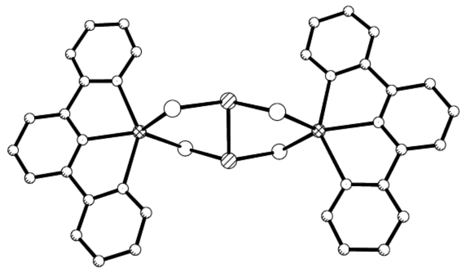


Fig. 17. Molecular structure of $[\{Mn(terpy)\}_2(\mu\text{-}As_2Se_4)]$ with tetradentate $As_2Se_4{}^{4-}$ ligands [6].

and contain $As_2Se_4{}^{4-}$ units that are linked by corner-sharing linear $As_3Se_7{}^{5-}$ anions (Fig. 16b). Crystallographic details are reported in the Experimental Section at the end of this article.

Two examples have been reported in which $As_2Se_4{}^{4-}$ units act as ligands in ternary selenidoarsenate anions. Such dipyramidal units exhibit a *trans* conformation in $Cs_4BiAs_3Se_7$ in which they chelate adjacent Bi atoms of the infinite ${}^{1}_{\infty}[\{Bi(AsSe_3)(\mu\text{-}As_2Se_4)\}^{4-}]$ chains through Se atoms from different pyramids [15]. A similar *trans* conformation and an analogous tetradentate coordination mode are also observed for the $As_2Se_4{}^{4-}$ ligands in $[\{Mn(terpy)\}_2(\mu\text{-}As_2Se_4)]$ [6], whose structure is depicted in Fig. 17. The former compound was prepared by methanolothermal reaction of Li_3AsSe_3, $BiCl_3$ and Cs_2CO_3 at 130 °C, the latter compound by heating $[MnCl_2(terpy)]$, As and Se in H_2O/tren (10 : 1) at 150 °C. A unique selenidoarsenate(II,IV) ligand $[AsSe_2(AsSe_3)]^{4-}$ containing a central As–As bond is present in the ${}^{2}_{\infty}[Ag_2(\mu\text{-}AsSe_4)(As_2Se_5)\}^{5-}]$ sheets of $K_5Ag_2As_3Se_9$ [32], which was also obtained by solvothermal reaction of K_3AsSe_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 dipyramidal $As_2E_4{}^{4-}$ building unit. Isolated $As_2Te_4{}^{4-}$ anions with respectively *gauche* and *trans* conformations have been reported for $Na_4As_2Te_4$ [89] and $K_4As_2Te_4$ [90]. A *trans* conformation is also observed for the same anion in $Rb_4As_2Te_4 \cdot en$, which was synthesized by extraction of an alloy of the same nominal composition with ethylenediamine [91]. The related *trans*-$[\{AsTe(Te_2)\}_2]^{4-}$ anions of $Cs_4As_2Te_6$ [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_2SO_3 with As_2Te_3 at 145 °C, higher temperatures (160–195 °C) lead to the isolation of the polytellurides Cs_2Te_5, Cs_2Te_{13}, Cs_4Te_{28} and Cs_3Te_{22} [95, 96], a finding that once again emphasizes the relative weakness of the As–Te bond. Two $As_2Te_4{}^{4-}$ anions are linked together through two shared Te atoms in the chair-shaped *cyclo*-$[As_4Te_6]^{4-}$ anions of $(Me_4N)_4As_4Te_6 \cdot 2en$ [93] and $[Ba(en)_4]_2As_4Te_6$ [94]. The former compound was prepared by electrochemical reduction of an As_2Te_3 electrode in an ethylenediamine solution of $(Me_4N)I$. On changing the cation source to $(Et_4N)I$, ${}^{1}_{\infty}[As_2Te_5{}^{2-}]$ chains result, in which alternating $As_2Te_4{}^{4-}$ dimers share their four Te atoms with square planar $TeTe_4{}^{6-}$ units [92]. No examples of ternary telluridoarsenate(II) anions have been reported.

Chalcogen-poor chalcogenidoarsenates $As_xE_y{}^{z-}$ with $y < x$ always contain more than one direct As–As bond. Cluster anions of the type $[As_{10}E_3]^{2-}$ are known for E = S – Te and are closely related to the Zintl anion $As_{11}{}^{3-}$ 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_4E_4 (E = S, Se) or As_2Te_3 with elemental K in NH_3 or ethylenediamine in the presence of Ph_4P^+ (E = Se [97], Te [98]) or $[K(2.2.2\text{-crypt})]^+$ cations (E = S [23]). The $[As_{11}Te]^{3-}$ anion of $[K(2.2.2\text{-crypt})]_3As_{11}Te \cdot en$ [99] is also related to the tris-homocubane-like $As_{11}{}^{3-}$ anion by addition of a single terminal Te atom. Two selenidoarsenate cluster anions of lower nuclearity (x = 6, 7) have been characterized in $[Mn(9\text{-ane-}N_3)_2]\ As_6Se_5$ (9-ane-N_3 = 1,4,7-triazacyclononane) [100] and $(Ph_4P)As_7Se_4$ [101], respectively, and one such anion of higher nuclearity (x = 12) in the compound

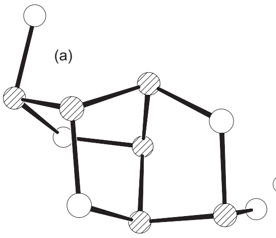


Fig. 18. The $[\mathrm{As_6Se_5}]^{2-}$ and $[\mathrm{As_{12}Se_4}]^{4-}$ cage-like anions of (a) $[\mathrm{Mn(9\text{-}ane\text{-}N_3)_2}]\mathrm{As_6Se_5}$ [100] and (b) $[\mathrm{Co(NH_3)_6}]_2\mathrm{As_{12}Se_4} \cdot 12\mathrm{NH_3}$ [102], respectively.

$[\mathrm{Co(NH_3)_6}]_2\mathrm{As_{12}Se_4} \cdot 12\mathrm{NH_3}$ [102]. The structure of the $[\mathrm{As_6Se_5}]^{2-}$ anion of $[\mathrm{Mn(9\text{-}ane\text{-}N_3)_2}]\mathrm{As_6Se_5}$, which was prepared by methanolothermal reaction of $[\mathrm{MnCl_3(9\text{-}ane\text{-}N_3)}]$ with $\mathrm{As_2Se_3}$ at 150 ℃ in the presence of $\mathrm{Cs_2CO_3}$, is depicted in Fig. 18a. It contains three fused five-membered $\mathrm{As_4Se}$ rings and can be regarded as being related to the bicyclic $\mathrm{As_4Se_6}^{2-}$ anion with two As atoms replacing endocyclic Se atoms and being bridged by an additional Se atom. Reduction of $\mathrm{As_4Se_4}$ with Na in liquid ammonia followed by precipitation with $\mathrm{CoBr_2}$ affords $[\mathrm{Co(NH_3)_6}]_2\mathrm{As_{12}Se_4} \cdot 12\mathrm{NH_3}$, whose unique cluster anion $[\mathrm{As_{12}Se_4}]^{4-}$ is shown in Fig. 18b. It consists of a central $\mathrm{As_{12}}$ 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 $\mathrm{AsS_4}^{3-}$ have been reported, *e. g.* $\mathrm{Na_3AsS_4} \cdot 8\mathrm{H_2O}$ [103], $\mathrm{K_3AsS_4}$ [104], $\mathrm{(NH_4)_3AsS_4}$ [105], and $\mathrm{Ba_3(AsS_4)_2} \cdot 7\mathrm{H_2O}$ [106]. The analogous $\mathrm{AsSe_4}^{3-}$ anion has been characterized in $[\mathrm{Li(NH_3)_4}]\mathrm{AsSe_4}$ [107], $\mathrm{Na_3AsSe_4} \cdot 9\mathrm{H_2O}$ [108], $\mathrm{Rb_3AsSe_4}$, $\mathrm{Cs_3AsSe_4}$ [109], and $\mathrm{Cs_3AsSe_4} \cdot \mathrm{H_2O}$ [110] among other compounds. The tetraselenidoarsenate(V) salts of the heavier alkali metal cations $\mathrm{Rb^+}$ and $\mathrm{Cs^+}$ were obtained by methanolothermal reaction of $A_2\mathrm{CO_3}$ (A = Rb, Cs) with $\mathrm{As_2Se_3}$ and Se at an appropriate molar ratio [109]. On changing the solvent from methanol to an equimolar $\mathrm{H_2O/CH_3OH}$ mixture the monohydrate $\mathrm{Cs_3AsSe_4} \cdot \mathrm{H_2O}$ [110] is formed, rather than $\mathrm{Cs_3AsSe_4}$. Reaction of the solvent with the thio- or selenidoarsenate(III) anions $\mathrm{As}E_3{}^{3-}$ present in methanolothermal reaction solutions affords substituted chalcogenidoarsenate(V) anions of the types $[\mathrm{As(CH_3)}E_3]^{2-}$ (E = S [111], Se [16]) and $[\mathrm{As(CH_3)_2Se_2}]^{-}$ [112] on leaving the mother liquor to slowly evaporate. The formation of $[\mathrm{As(CH_3)}E_3]^{2-}$ anions requires methanol reduction according to (6)

$$\mathrm{As}E_3{}^{3-} + \mathrm{CH_3OH} \rightleftharpoons [\mathrm{As(CH_3)}E_3]^{2-} + \mathrm{OH^-} \quad (6)$$

Pertinent examples of other substituted selenidoarsenate(V) anions are found in the salts $[\mathrm{K(2.2.2\text{-}crypt)}]_2$-$[\mathrm{As(CH_3CN)Se_3}]$ [113] and $\mathrm{(pipH)[AsPh_2Se_2]}$ [114]. As to be expected, the potential telluridoarsenate(V) anion $\mathrm{AsTe_4}^{3-}$ is unknown.

Tetrahedral $\mathrm{AsS_4}^{3-}$ ligands have been incorporated into the ternary coinage metal thioarsenate(V) polyanions of compounds such as $\mathrm{NH_4[Ag_2AsS_4]}$ [115], $\mathrm{(NH_3CH_2CH_2NH_3)[AgAsS_4]}$ [116], $\mathrm{K[Ag_2AsS_4]}$ [117], $\mathrm{Cs_2[AgAsS_4]}$ [118], and $\mathrm{K_2[AuAsS_4]}$ [119]. $\mathrm{Rb_8[Cd_2(AsS_4)_2(\mu\text{-}AsS_5)_2]}$ was obtained from a rubidium polythioarsenate flux at 500 ℃ [120] and contains a dinuclear anion in which the Cd atoms are bridged by a unique tetradentate $[\mathrm{AsS_3(S_2)}]^{3-}$ ligand. The $[\mathrm{Mn_2(AsS_4)_2(\mu\text{-}AsS_4)_2}]^{8-}$ anions of the similarly prepared compounds $A_8[\mathrm{Mn_2As_4S_{16}}]$ (A = Rb, Cs) [120] exhibit a comparable dinuclear structure but in this case $\mathrm{AsS_4}^{3-}$ ligands exhibit adequate bite angles to allow the bridging of the smaller Mn atoms in an analogous μ-$1\kappa^2\mathrm{S}^1,\mathrm{S}^2:2\kappa^2\mathrm{S}^2,\mathrm{S}^3$ mode. Examples have also recently been reported of $\mathrm{AsS_4}^{3-}$ anions acting as ligands to $\{\mathrm{Mn(amine)}\}^{2+}$ and $\{\mathrm{Mn(imine)}\}^{2+}$ fragments in hydrothermally synthesized compounds, and to lanthanide metals in the phases $\mathrm{K_3}[Ln\mathrm{(AsS_4)_2}]$ (Ln = Nd, Sm, Gd [121]), which were obtained in potassium thioarsenate fluxes. The tetrathioarsenate(V) anion adopts a chelating mode in the anion of $[\mathrm{Mn(en)_3}]_2[\{\mathrm{Mn(en)_2}\}\mathrm{AsS_4}][\mathrm{As_3S_6}]$ [13], a bridging μ_2-$1\kappa^2\mathrm{S}^1,\mathrm{S}^2:2\kappa\mathrm{S}^2$ mode in the infinite chains of $[\mathrm{Mn(dien)_2}][\{\mathrm{Mn(dien)}\}\mathrm{AsS_4}]_2 \cdot 4\mathrm{H_2O}$ [13] and a hexadentate μ_3-$1\kappa^2\mathrm{S}^1,\mathrm{S}^2:2\kappa^2\mathrm{S}^2,\mathrm{S}^3:3\kappa^2\mathrm{S}^3,\mathrm{S}^4$ mode in the 1D polyanions of $[\{\mathrm{Mn(2,2'\text{-}bpy)}\}_3(\mu_3\text{-}\mathrm{AsS_4})_2] \cdot \mathrm{H_2O}$ [5]. A μ_3-$\mathrm{AsS_4}^{3-}$ bridging ligand has been observed in the lanthanide thioarsenates $\mathrm{K_3[Ln(AsS_4)_2]}$ [121].

In striking contrast to the ternary thioarsenate(V) anions, very few examples of compounds containing $\mathrm{AsSe_4}^{3-}$ ligands have been reported. However, μ_2-bridging $\mathrm{AsSe_4}^{3-}$ ligands are present in the $^2_\infty[\{\mathrm{Ag_2(As_2Se_5)(AsSe_4)}\}^{5-}]$ layers of the methanolothermal phase $\mathrm{K_5[Ag_2As_3Se_9]}$ [32], which also contain the mixed valent $\mathrm{As_2Se_5}^{4-}$ anion, already discussed in Section 4. A μ_2-$1\kappa^2\mathrm{Se}^1,\mathrm{Se}^2:2\kappa\mathrm{Se}^3$ mode is adopted by the tetrahedral selenidoarsenate(V) ligand in the infinite chains of the lanthanide compounds $^1_\infty[Ln\mathrm{(dien)_2}(\mu_2\text{-}\mathrm{AsSe_4})]$ (Ln = Nd, Sm) [122], which

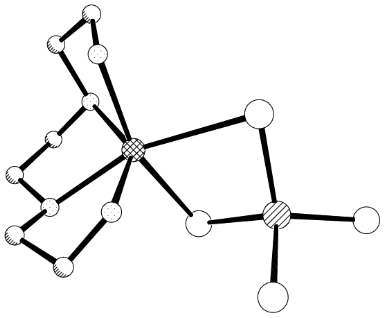


Fig. 19. The κ^2Se coordination mode of the $AsSe_4^{3-}$ anion in Cs[{Mn(trien)}$AsSe_4$] · CH_3OH (this work).

were synthesized by reaction of As_2O_3 with Se and Nd_2O_3 or Sm_2O_3 in dien at 140 °C. We now report the first example of a transition metal complex containing an $AsSe_4^{3-}$ ligand. Cs[{Mn(trien)}$AsSe_4$] · CH_3OH was obtained in low yield by methanolothermal reaction of $MnCl_2$, trien, As and Se in the presence of Cs_2CO_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′ angle of 81.58(8)° and one typical (2.684(3) Å) and one long (2.881(3) Å) Mn–Se bond.

Conclusions

Despite the structural restrictions imposed by the reluctancy 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 $As_2E_4^{4-}$ 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-}, $As_2S_5^{4-}$ and *cyclo*-$[As_3S_6]^{3-}$ 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 $AAsS_2$, $A_2As_4S_7$, $A_2As_6S_{10}$ and $A_2As_8S_{13}$ (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 $^1_\infty[AsSe_2{}^-]$ found in the alkali metal phases $AAsSe_2$ (A = Na–Cs). The polymeric $^1_\infty[As_4Se_7{}^{2-}]$ ligands of $^1_\infty$[{Mn(tren)}As_4Se_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 $^1_\infty[AsSe^{3-}]$ and *cyclo*-$[As_2Se_6]^{2-}$, no thioarsenate(III) anions containing AsE_3^{3-} pyramids linked by homonuclear *E*–*E* bonds are currently known.

Infinite $^1_\infty[AsSe^{3-}]$ chains have been characterized in the hydrothermally synthesized phases $KAsSe_3 \cdot H_2O$ and $AAsSe_3 \cdot 0.5H_2O$ (A = Rb, Cs) [39]. The chair-shaped *cyclo*-$[As_2Se_6]^{2-}$ 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_4N^+ [68], Ph_4P^+ [69, 73] and $[M(en)_3]^{2+}$ (M = Mn, Fe) [30].

c) Whereas the $As_4S_6^{2-}$ anion represents the only currently known example of a thioarsenate species with a homonuclear As–As bond, not only the analogous $As_4Se_6^{2-}$ anion but also a variety of other binary and ternary selenidoarsenates containing the characteristic $As_2E_4^{4-}$ unit have been prepared.

The dipyramidal selenidoarsenate(III) moiety $As_2Se_4^{4-}$ has been characterized as a building unit in the $^1_\infty[As_4Se_6{}^{2-}]$ and $^1_\infty[As_5Se_9{}^{5-}]$ chains of $Cs_2As_4Se_6$ [16] and $Cs_5As_5Se_9$, respectively, and as a tetradentate μ_2-$1\kappa^2Se^1,Se^3:2\kappa^2Se^2,Se^4$ ligand in $Cs_4BiAs_3Se_7$ [15] and [{Mn(terpy)}$_2As_2Se_4$] [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*-$[As_2Te_6]^{2-}$ anion of $(Ph_4P)_2As_2Te_6$ [76] and [K(2.2.2-crypt)]$_2As_2Te_6$ [77] with its $AsTe_3^{3-}$ units linked by Te–Te bonds. In contrast, the dipyramidal $As_2Te_4^{4-}$ species has been characterized not only as a discrete anion in alkali metal salts $A_4As_2Te_4$ (A = Na–Rb [89 – 91]) but also as a building unit in the binary $^1_\infty[As_2Te_5{}^{2-}]$, $As_2Te_6^{4-}$ and *cyclo*-$[As_4Te_6]^{4-}$ anions [92 – 94]. Of these, the infinite $^1_\infty[As_2Te_5{}^{2-}]$ chain of $(Et_4N)_2As_2Te_5$ and the dinuclear *trans*-$[\{AsTe(Te_2)\}_2]^{4-}$ anion of $Cs_4As_2Te_6$ appear to represent the only examples of chalcogenidoarsenate species simultaneously displaying As–*E*, As–As and *E*–*E* bonds.

Experimental Section

$Cs_5As_5Se_9$

300 mg $CsAsSe_3 \cdot 0.5H_2O$ (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 $Cs_5As_5Se_9$ in about 3 % yield (relative to As) together with black $Cs_2As_4Se_6$ [16] (32 %), red $Cs_4As_4Se_8$ [31] (10 %) and black Cs_2Se_5. Crystals of $Cs_5As_5Se_9$ were separated under a polarizing microscope. $Cs_5As_5Se_9$ (M = 1749.8 $\mathrm{g\,mol^{-3}}$) 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) $Å^3$, Z = 4, D_{calc} = 4.40 $\mathrm{g\,cm^{-3}}$, μ = 24.5 $\mathrm{mm^{-1}}$, $F(000)$ = 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 $0.15 \times 0.11 \times 0.10$ $\mathrm{mm^3}$ using graphite-monochromated $\mathrm{Mo}K_\alpha$ 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 $F_0{}^2$ using SHELX-97 [123] to R_1 = 0.123 [$I \geq 2\sigma(I)$] and wR_2 = 0.321 for all 2371 symmetry-independent reflections ($0 \leq h \leq 9, -32 \leq k \leq 0, 0 \leq l \leq 14$) from 2371 measured reflections. All atoms were assigned anisotropic displacement parameters. The residual electron density values were 2.02 and 2.71 $\mathrm{e\,Å^{-3}}$.

$Cs[\{Mn(trien)\}(AsSe_4)] \cdot CH_3OH$

79.3 mg of Se (1.0 mmol), 37.6 mg of As (0.5 mmol), 63.4 mg of $MnCl_2$ (0.5 mmol), 0.075 mL of trien (0.5 mmol) and 165.0 mg of Cs_2CO_3 (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 $Cs[\{Mn(trien)\}AsSe_4)] \cdot CH_3OH$ in low yield (5 %). $C_7H_{22}AsCsMnN_4OSe_4$ (M = 756.9 $\mathrm{g\,mol^{-1}}$)) crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with a = 7.968(2), b = 11.359(5), c = 22.110(6) Å, β = 95.74(1)°, V = 1991.3(12) $Å^3$, Z = 4, D_{calc} = 2.53 $\mathrm{g\,cm^{-3}}$, μ = 11.4 $\mathrm{mm^{-1}}$, $F(000)$ = 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 $0.45 \times 0.26 \times 0.23$ $\mathrm{mm^3}$ using graphite-monochromated $\mathrm{Mo}K_\alpha$ radiation (λ = 0.71073 Å) and corrected using ψ scans for absorption. The structure was solved by Direct Methods and refined for 182 parameters against $F_0{}^2$ using SHELX-97 [123] to R_1 = 0.075 [$I \geq 2\sigma(I)$] and wR_2 = 0.253 for all 3467 symmetry-independent reflections ($-1 \leq h \leq 9, -13 \leq k \leq 1, -26 \leq l \leq 26$) 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 $\mathrm{e\,Å^{-3}}$.

CSD 421375 ($Cs_5As_5Se_9$) and CCDC 761656 ($Cs[\{Mn(trien)\}(AsSe_4)] \cdot CH_3OH$) 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.

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