Synthesis and Crystal Structure of K_3AsSe_4 and $K_4As_2Se_5$ Containing $[AsSe_4]^{3-}$ Anions and a Novel $[As_2Se_5]^{4-}$ Isomer Featuring an As–As Bond

Prashanth W. Menezes and Thomas F. Fässler

Department Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Reprint requests to Prof. Dr. Thomas F. Fässler. E-mail: thomas.faessler@lrz.tum.de

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Two novel selenoarsenates, K_3AsSe_4 and $K_4As_2Se_5$, were synthesized by the mild solvothermal reaction of potassium carbonate and arsenic and selenium powder in the presence of superheated ethylenediamine and structurally characterized by single-crystal X-ray diffraction. K_3AsSe_4 crystallizes in the orthorhombic space group *Pnma* (no. 62) with $a = 9.4169(4)$, $b = 10.9695(5)$, $c = 9.7568(8)$ Å, $Z = 4$ and $V = 1007.86(10)$ Å^3 and contains $[AsSe_4]^{3-}$ anions with pentavalent arsenic. $K_4As_2Se_5$ crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with $a = 7.6167(2)$, $b = 22.8733(4)$, $c = 8.4687(2)$ Å, $\beta = 107.241(2)°$, $Z = 4$ and $V = 1409.14(5)$ Å^3, and shows isolated $[As_2Se_5]^{4-}$ anions. The most prominent feature of the latter anions is the presence of arsenic in two different formal oxidation states (+4/+2) due to the presence of an As–As bond.

Key words: Solvothermal Synthesis, Arsenic, Selenium, Selenoarsenate, Crystal Structure

Introduction

The synthesis of compounds with main-group chalcogenides has been an extremely active area in solid-state and materials chemistry [1 – 3]. Over the past few years, the mild solvothermal technique has proved to open convenient synthetic routes to chalcogenidoarsenates which are often inaccessible *via* the traditional solution approach [4]. Focusing on selenoarsenates, a wide variety of isolated $[As_xSe_y]^{n-}$ anions have been reported with diverse connectivity patterns of arsenic and selenium atoms as well as with various formal oxidation states of arsenic [4]. These anions include the selenium-rich species $[AsSe_3]^{3-}$ [5, 6], $[AsSe_4]^{3-}$ [7 – 10], $[AsSe_6]^{-}$ [11, 12], $[AsSe_8]^{-}$ [12], $[As_2Se_4]^{2-}$ [6], $[As_2Se_5]^{4-}$ [13, 14], $[As_2Se_6]^{2-}$ [11, 12, 15 – 19], $[As_3Se_6]^{2-}$ [19, 20], $[As_4Se_6]^{2-}$ [15, 21], and $[As_4Se_8]^{2-}$ [22], and the selenium-poor anions $[As_6Se_5]^{2-}$ [23], $[As_7Se_4]^{-}$ [24], $[As_{10}Se_3]^{2-}$ [25], and $[As_{12}Se_4]^{4-}$ [26], the structures of which are of cluster or cage type. In most cases the anions are charge-balanced by alkali/alkaline earth metal cations, but organoelement cations or transition metal complex cations were also employed.

Recently, we extended our investigations of Zintl ions of group 14 and 15 elements and related intermetalloid clusters [27 – 30] to their reactions under solvothermal conditions in superheated and supercritical amines [31]. We also studied the reactions of group 15 elements with the higher chalcogens in superheated ethylenediamine aiming at the synthesis of heteroatomic Zintl clusters using potassium carbonate as mineralizer. In the present contribution we report the synthesis and crystal structure of the two novel selenoarsenates K_3AsSe_4 and $K_4As_2Se_5$ obtained in superheated ethylenediamine *via* the solvothermal route. Both compounds show a remarkable difference in the formal oxidation state of the arsenic atoms: K_3AsSe_4 with its pentavalent arsenic completes the series of selenoarsenate $[AsSe_4]^{3-}$ anions charge-balanced by alkali metals, and $K_4As_2Se_5$ is the first compound with an isolated $[As_2Se_5]^{4-}$ unit with a direct As–As bond and thus mixed-valent As atoms with the formal oxidation states +4 and +2.

Results and Discussion

K_3AsSe_4 crystallizes in the centrosymmetric space group *Pnma* (no. 62) with four formula units per unit cell (Table 1). The crystal structure is composed of discrete tetrahedral selenoarsenate(V) anions $[AsSe_4]^{4-}$ (Fig. 1) that are surrounded by potassium cations. As expected, the arsenic atom is tetrahedrally coordinated by four Se atoms with As–Se distances ranging from 2.3068(5) to 2.3267(4) Å and Se–As–Se angles between 108.472(12) and 111.488(17)°. These data are in accordance with the distances and angles found in Rb_3AsSe_4, Cs_3AsSe_4 and other related structures [7 – 10].

The structure contains two crystallographically independent K^+ cations (Fig. 2). The ions K1 are coordinated by seven Se atoms of five symmetry-related tetrahedral $[AsSe_4]^{4-}$ anions, whereas K2 is also coordinated by seven Se atoms, but these belong to only four symmetry-related $[AsSe_4]^{4-}$ anions. K1 and K2 both exhibit one short [3.2300 and 3.2541 Å], four medium [3.3373–3.4367 Å] and two long [3.6057–3.7550 Å] K–Se distances. The overall structure of K_3AsSe_4 is depicted in Fig. 3.

Considering the tetraselenoarsenates(V) with discrete isolated $[AsSe_4]^{4-}$ anions, only a restricted number of examples is known, including $[Li(NH_3)_4]_3AsSe_4$ [7], $Na_3AsSe_4 \cdot 9H_2O$ [8], Rb_3AsSe_4 [10], Cs_3AsSe_4 [10], and $Cs_3AsSe_4 \cdot H_2O$ [9], while substituted selenoarsenate(V) anions are limited to $Na_3(AsO_3Se) \cdot 12H_2O$ [8], $K(2.2.2.crypt)]_2[As(CH_2CN)Se_3]$ [32], $(pipH_2)[AsPh_2Se_2]$ [33], $Cs[As(CH_3)_2Se_2]$ [34], and $Cs_2[As(CH_3)Se_3] \cdot 2H_2O$ [35]. K_3AsSe_4 is thus a new member in the still limited series of alkali tetraselenoarsenates(V).

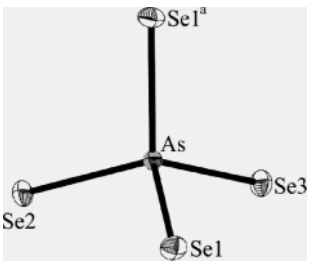

Fig. 1. Crystal structure of the isolated $[AsSe_4]^{3-}$ anion in K_3AsSe_4 with crystallographic atom labeling adopted. The displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are given in Table 2.

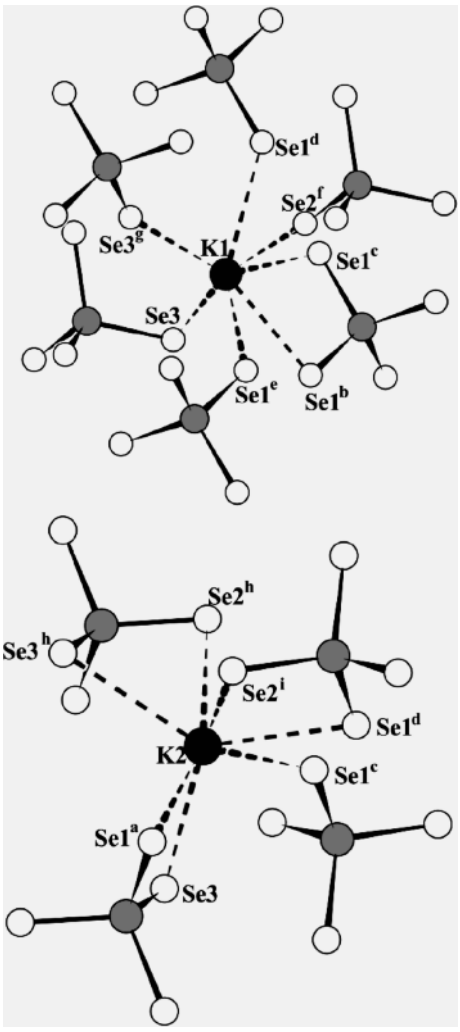

Fig. 2. Coordination sphere of the K^+ cations in the crystal structure of K_3AsSe_4 with atom labeling adopted. K1 ions are coordinated by seven Se atoms of five tetrahedral symmetry-related $[AsSe_4]^{4-}$ anions whereas K2 is coordinated by seven Se atoms of four symmetry-related $[AsSe_4]^{4-}$ anions. Symmetry codes are given in Table 2.

$K_4As_2Se_5$ crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with four formula units per cell (Table 1). The crystal structure analysis revealed that the structure is built from novel isolated selenoarsenate(IV\II) anions $[As_2Se_5]^{4-}$ (Fig. 4) which are surrounded by K^+ cations. In this anion As1 is coordinated by three Se atoms while As2 is bonded to only two Se atoms. As1 and As2 are linked by a direct As–As bond. The formal oxidation state of the tetrahedrally tetracoordinated atom As1 can be

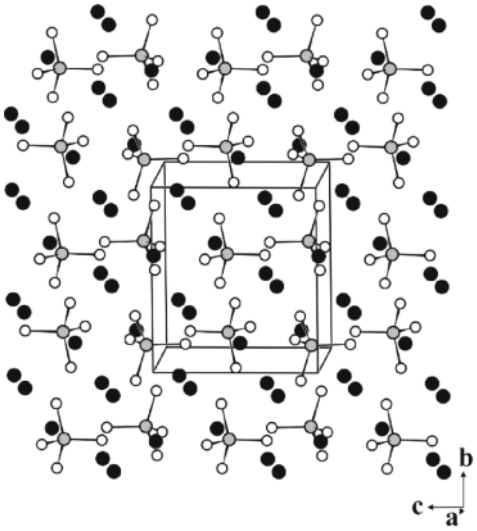

Fig. 3. Crystal structure of K_3AsSe_4 composed of $[AsSe_4]^{4-}$ anions and K^+ cations. Atom color codes: K filled black circles, As filled gray circles, Se open circles.

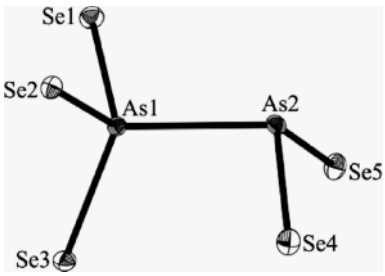

Fig. 4. Crystal structure of the isolated $[As_2Se_5]^{4-}$ anion in $K_4As_2Se_5$ with atom labeling adopted. The displacement ellipsoids are drawn at the 50 % probability level.

assigned as 4+ and that of the tricoordinated As2 atom as 2+ which leads to a total charge of 4− for the anion. There are similarities to fragments of the layered structure of $K_5[Ag_2As_3Se_9]$ [36]. The As–Se bond lengths and the Se–As–Se angles range from 2.3204 to 2.3509 Å and from 108.52 to 111.68°, respectively. The As–As distance is 2.5000(5) Å. The bond lengths and angles of $[As_2Se_5]^{4-}$ are comparable to those observed in other selenoarsenates [6, 11 – 26]. The $[As_2Se_5]^{4-}$ anion can also be seen as a staggered structure which is closely related to methylamine (CH_3NH_2). The dihedral Se–As–As–Se angles for the $[As_2Se_5]^{4-}$ anion are in the range of 115.5 to 123.9°, and an almost staggered conformation is given by

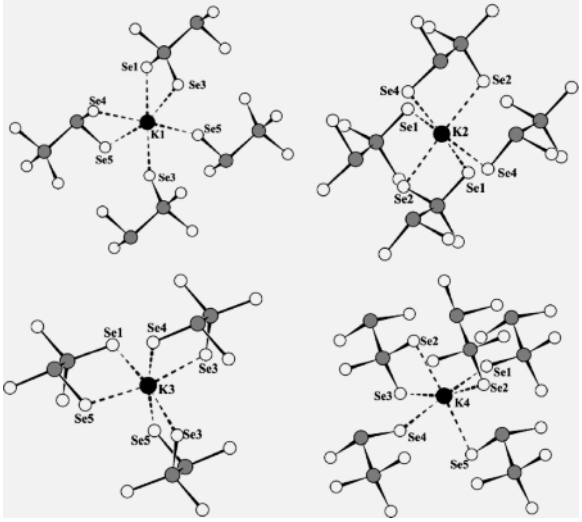

Fig. 5. Coordination sphere of the K^+ cations in the crystal structure of $K_4As_2Se_5$ with atom labeling adopted. All four K^+ cations accommodate six Se atoms in their coordination sphere and are interconnected to four (K1 and K2), three (K3) and five (K4) $[As_2Se_5]^{4-}$ anions.

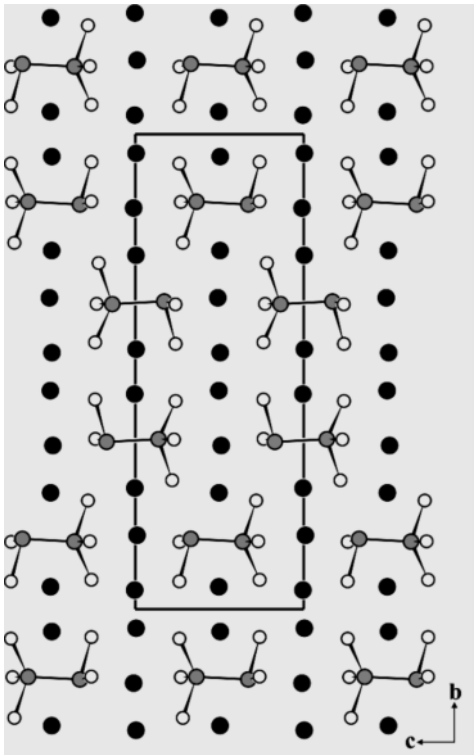

Fig. 6. Crystal structure of $K_4As_2Se_5$ built from $[As_2Se_5]^{4-}$ anions and K^+ cations. Atom color codes: K filled black circles, As filled gray circles, Se open circles.

Table 1. Summary of crystal data and refinement parameters for K_3AsSe_4 and $K_4As_2Se_5$.

	K_3AsSe_4	$K_4As_2Se_5$
Empirical formula	AsK_3Se_4	$As_2K_4Se_5$
Formula wt., g mol^{-1}	508.06	701.04
T, K	150(1)	150(1)
λ, Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pnma* (no. 62)	$P2_1/n$ (no. 14)
a, Å	9.4169(4)	7.6167(2)
b, Å	10.9695(5)	22.8733(4)
c, Å	9.7568(8)	8.4687(2)
β, deg	90	107.241(2)
V, Å^3	1007.86(10)	1409.14(5)
Z	4	4
$D_{calcd.}$, g cm^{-3}	3.35	3.30
Abs. coef., mm^{-1}	19.9	19.0
$F(000)$, e	904	1248
θ range, deg	3.01–27.48	2.94–27.50
Index ranges	$-9 \le h \le 12$	$-9 \le h \le 9$
	$-14 \le k \le 14$	$-29 \le k \le 29$
	$-12 \le l \le 12$	$-6 \le l \le 11$
Refl. collected/ indep./R_{int}	13853/1220/0.032	15642/3235/0.037
Completeness, %	99.9	99.9
Ref. parameters	44	101
$R1/wR2$ [$I > 2\sigma(I)$]	0.015/0.034	0.020/0.044
$R1/wR2$ (all data)	0.018/0.035	0.031/0.045
Goodness-of-Fit	1.163	1.090
Largest diff. peak/ hole, e Å^{-3}	0.78/ − 0.577	1.10/ − 0.75

Table 2. Selected interatomic distances (Å) and angles (deg) for K_3AsSe_4 (standard deviation in units of the last significant figure in parentheses).

K1–Se1^b	3.4004(7)	K2–Se1^a	3.3755(6)
K1–Se1^c	3.4004(7)	K2–Se1^c	3.6057(6)
K1–Se1^d	3.7550(4)	K2–Se1^d	3.4085(6)
K1–Se1^e	3.7550(4)	K2–Se2^h	3.2541(6)
K1–Se2^f	3.2300(9)	K2–Se2^i	3.3373(6)
K1–Se3	3.3868(8)	K2–Se3	3.4360(5)
K1–Se3^g	3.4367(9)	K2–Se3^h	3.6635(6)
As1–Se1^a	2.3109(3)	Se1^a–As1–Se1	111.49(2)
As1–Se1	2.3109(3)	Se1^a–As1–Se3	109.48(1)
As1–Se2	2.3068(5)	Se1–As1–Se3	109.48(1)
As1–Se3	2.3267(4)	Se2–As1–Se1^a	108.47(1)
		Se2–As1–Se1	108.47(1)
		Se2–As1–Se3	109.42(2)

Symmetry codes: ^{a} $x, -y+1/2, z$; ^{b} $x-1/2, y, -z+1/2$; ^{c} $x-1/2, -y+1/2, -z+1/2$; ^{d} $-x+1/2, y+1/2, z-1/2$; ^{e} $-x+1/2, -y, z-1/2$; ^{f} $x, y, z-1$; ^{g} $x+1/2, y, -z+1/2$; ^{h} $-x, -y+1, -z+1$; ^{i} $-x+1/2, -y+1, z-1/2$.

Table 3. Selected interatomic distances (Å) and angles (deg) for $K_4As_2Se_5$ (standard deviation in units of the last significant figure in parentheses).

K1–Se1	3.3195(9)	K3–Se1	3.3101(8)
K1–Se3	3.2377(8)	K3–Se3^c	3.3415(8)
K1–Se3^a	3.4702(9)	K3–Se3^f	3.3041(8)
K1–Se4^b	3.3060(9)	K3–Se4^f	3.2986(9)
K1–Se5^b	3.2173(8)	K3–Se5^c	3.3151(9)
K1–Se5^c	3.3815(9)	K3–Se5	3.3123(8)
K2–Se1	3.4770(9)	K4–Se1^g	3.7154(9)
K2–Se1^d	3.4175(9)	K4–Se2^h	3.3240(9)
K2–Se2	3.2818(9)	K4–Se2^i	3.2380(9)
K2–Se2^e	3.3058(9)	K4–Se3^i	3.3372(9)
K2–Se4^b	3.4958(9)	K4–Se4^f	3.4884(9)
K2–Se4^e	3.4285(9)	K4–Se5	3.3622(9)
As1–Se1	2.3204(5)	Se1–As1–Se2	109.104(19)
As1–Se2	2.3273(5)	Se1–As1–Se3	111.676(19)
As1–Se3	2.3290(5)	Se2–As1–Se3	110.241(18)
As2–Se4	2.3350(5)	Se4–As2–Se5	108.515(19)
As2–Se5	2.3509(5)		
As1–As2	2.5000(5)		

Symmetry codes: ^{a} $-x, -y, -z$; ^{b} $x, y, z-1$; ^{c} $-x+1, -y, -z+1$; ^{d} $x-1/2, -y+1/2, z-1/2$; ^{e} $x+1/2, -y+1/2, z-1/2$; ^{f} $x+1, y, z$; ^{g} $x, y, z+1$; ^{h} $x+1/2, -y+1/2, z+1/2$; ^{i} $x+1, y, z+1$.

the angles in the range of 53.1 and 67.3° which are both comparable to the situation observed in methylamine [37].

All four potassium cations contain six atoms in their coordination sphere (Fig. 5) and are connected to four (K1 and K2), three (K3) and five (K4) $[As_2Se_5]^{4-}$ anions with K–Se distances in the respective range of 3.2173(8)–3.4702(9) Å (K1), 3.2818(9)–3.4958(9) Å (K2), 3.2986(9)–3.3415(8) Å (K3), and 3.2380(9)–3.7154(9) Å (K4). The complete crystal structure is presented in Fig. 6.

Discrete selenoarsenate(III) $[As_2Se_5]^{4-}$ anions have also been observed in $[M(en)_3]_2[As_2Se_5]$ (M = Mn, Co) [13, 14], but consist of two vertex-sharing $[AsSe_3]^{3-}$ units (Fig. 7a). Surprisingly, the structure of the selenoarsenate(IV\II) anion $[As_2Se_5]^{4-}$ in $K_4As_2Se_5$ (Fig. 7b) is thus completely different. The two different $[As_2Se_5]^{4-}$ anions can best be described as structural isomers formally related through a disproportionation from oxidation state +3 for the As atoms in the isomer of Fig. 7a to the mixed-valent anion shown in Fig. 7b with oxidation states +4 and +2 for the As atoms.

K_3AsSe_4 and $K_4As_2Se_5$ both are structurally related to the layered compound $K_5[Ag_2As_3Se_9]$ [36], which was obtained by the reaction of K_3AsSe_3 with $AgBF_4$ in superheated methanol at 383 K. It consists

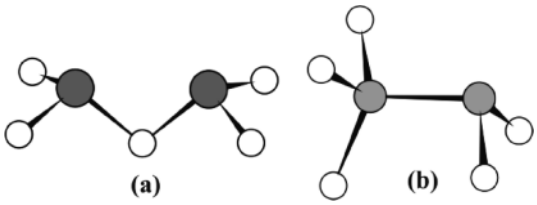

Fig. 7. Crystal structure of the isolated $[As_2Se_5]^{4-}$ anion (a) in $[M(en)_3]_2[As_2Se_5]$ (M = Mn, Co) and (b) in $K_4As_2Se_5$. Atom color codes: As filled gray circles, Se open circles.

of chains of the composition $[Ag_3As_3Se_9]^{2-}$ built from $[AsSe_4]^{3-}$ and $[As_2Se_5]^{4-}$ units which are connected to Ag atoms with the formation of rings. The structural fragments $[AsSe_4]^{3-}$ and $[As_2Se_5]^{4-}$ correspond precisely to the units found in K_3AsSe_4 and $K_4As_2Se_5$ now obtained from K_2CO_3, and As and Se powder in the presence of superheated ethylenediamine at 443 K. This result shows the new opportunities offered by the solvothermal techniques.

Experimental Section

All materials were handled in an argon atmosphere using a glove box with moisture and oxygen levels below 1 ppm. Ethylenediamine was dried over Na/CaH_2 and freshly distilled prior to use.

Syntheses of K_3AsSe_4 and $K_4As_2Se_5$

Single crystals of K_3AsSe_4 and $K_4As_2Se_5$ were obtained from a mixture of K_2CO_3 (138 mg, 1 mmol), As (75 mg, 1 mmol) and Se powder (240 mg, 3 mmol) in ethylenediamine (5 mL). The reactants were loaded into a Teflon-lined autoclave with an inner volume of 20 mL (filling degree approx. 25 %). The sealed autoclave was heated at 443 K for 12 d and then cooled to room temperature. The reaction led to a mixture of red crystals of K_3AsSe_4 and black crystals of $K_4As_2Se_5$ with dimensions up to 0.1 mm. The total yield based on Se was approximately 80 %.

EDX analyses

Single crystals of K_3AsSe_4 and $K_4As_2Se_5$ were investigated by energy dispersive X-ray (EDX) analyses for a semi-quantitative determination of the elements present on the sample surfaces (K, As, Se). The measurements were carried out on a JEOL-SEM 5900LV spectrometer. The approximate atomic ratios obtained for K/As/Se (3 : 1 : 4 and 4 : 2 : 5, respectively) reflect the compositions determined by the single-crystal X-ray structure determinations. No other elements heavier than Na were detected.

Single-crystal structure determinations

Diffraction data of K_3AsSe_4 and $K_4As_2Se_5$ were collected on an Oxford Xcalibur3 diffractometer with MoK_α radiation (λ = 0.71073 Å) at a temperature of 150 K. Suitable single crystals were selected and fixed in a capillary using perfluoropolyalkyl ether. The capillary was sealed and transferred to the diffractometer. The crystal structures were solved by Direct Methods using the program SHELXS-97 [38a]. Refinements were performed with the program SHELXL [38b] included in the program package WINGX [38c]. Based on the systematic absences, the space group was determined to be orthorhombic *Pnma* (no. 62) for K_3AsSe_4 and monoclinic $P2_1/n$ (no. 14) for $K_4As_2Se_5$. A summary of crystallographic data, refinement parameters, selected bond lengths and bond angles are listed in Tables 1–3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD-424533 (K_3AsSe_4) and CSD-424534 ($K_4As_2Se_5$).

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