

Tetrapotassium nonastannide, K_4Sn_9

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In K_4Sn_9 , which crystallizes with a new structure type, the Sn atoms form isolated Wade *nido*- $[Sn_9]^{4-}$ clusters of approximate C_{4v} symmetry (monocapped square antiprisms), with Sn—Sn distances ranging from 2.9264 (9) to 3.348 (1) Å. The cluster anions are separated by K^+ cations and are in a hexagonal close-packed arrangement.

Comment

Binary zintl phases of the composition $A_4M_9^{IV}$ (A^I : alkaline metal; M^{IV} : Si, Ge, Sn or Pb) were observed for the first time by Zintl himself (Zintl *et al.*, 1931). While the isolated $[M_9^{IV}]^{4-}$ clusters are well known in solution and were stabilized and characterized in the solid state with a variety of counter-ions and solvates [for example, as $Rb_4Ge_9(en)$, where en is ethylenediamine (Somer *et al.*, 1998)], only a small number of pure binary intermetallic compounds with this type of nonatetrelide cluster have been structurally characterized. For the composition A_4M_9 , the crystal structures are known for only the two plumbides K_4Pb_9 (Queneau & Sevov, 1998) and Cs_4Pb_9 (Todorov & Sevov, 1998), and the corresponding germanides ($A = K$: Schnering *et al.*, 1997; $A = Rb$ or Cs : Queneau & Sevov, 1997). For silicides and stannides, no crystal data have been reported so far, though for the latter compounds, vibrational spectra have been published (Schnering *et al.*, 1997).

Isolated $[M_9]^{4-}$ clusters (besides two zintl $[M_4]^{4-}$ anions) are also present in the binary compounds of composition $A_{12}M_{17}$, presumably reported as A_2M_3 in the published phase diagrams. Compounds of this type are described for the elemental A/M combinations Rb/Si and K/Sn (Queneau *et al.*, 1998), Na/Ge and K/Ge [Schnering *et al.*, 1997; MgZn₂ arrangement of M_9 (Mg) and M_4 (Zn) building units] and Rb/Sn (Hoch *et al.*, 1998; Hoch & Röhr, 2000; MgCu₂ arrangement of the anions), but all the crystal structure determinations suffer from problems with crystal quality, structural disorder, superstructures or large unit cells. Recently, Sevov and co-workers have prepared a series of new mixed-alkaline metal stannides, for example, with *arachno*- $[Sn_8]^{6-}$ clusters in

$K_4Li_2Sn_8$ (Bobev & Sevov, 2000), but crystal data for simple binary stannides (A_4Sn_9) are still missing (Fässler & Hoffmann, 1999).

The binary alkaline metal stannide K_4Sn_9 was prepared from stoichiometric mixtures of the elements at 1280 K. The very air-sensitive crystals have a silver metallic luster. The crystal structure contains $[Sn_9]^{4-}$ clusters, which are depicted in Fig. 1. These have no special site symmetry but are of approximate C_{4v} point-group symmetry and can best be described as monocapped square antiprisms. Thus, they are, in accordance with Wade's rules, electron precise *nido* clusters with 11 skeleton electron pairs. Because of the approximate high symmetry, the Sn—Sn distances in the cluster can be sorted into four groups (*A* to *D*; see Fig. 1). The Sn—Sn distances between four- and five-bonded atoms [*A*: 2.9264 (9)–2.9955 (9) Å; *C*: 2.9299 (8)–3.0163 (8) Å], and between two four-bonded atoms [*D*: 2.9475 (8)–3.0008 (8) Å] are within the ranges of values found in other Zintl phases [for example, in KSn : 2.96–2.98 Å (Hewaidy *et al.*, 1964)]. The intra-cluster distances *B* between two five-bonded Sn atoms are, with values in the range 3.1243 (9)–3.348 (1) Å, somewhat longer. A comparable general pattern can be found in all compounds with fully isolated $[Sn_9]^{4-}$ cluster anions. The bond angles are also close to the ideal values of a monocapped square antiprism [α : 64.70 (2)–69.30 (2)°; β , δ and ε : 56.081 (18)–60.985 (18)°; γ and φ : 87.93 (2)–91.49 (2)°].

The clusters are separated by the K^+ counter-cations, which are coordinated by 7–10 Sn atoms, with $K \cdots Sn$ distances in the range 3.550 (2)–4.230 (2) Å. As the shortest inter-cluster $Sn \cdots Sn$ distance is 4.1622 (9) Å, a direct interaction between the clusters (as observed, for example, in K_4Pb_9) can be ruled out. Fig. 2 shows the arrangement of the Sn_9 anions in the unit cell. The clusters form distorted hexagonal close-packed layers in the *bc* plane, which are stacked in the sequence ...*AB*...

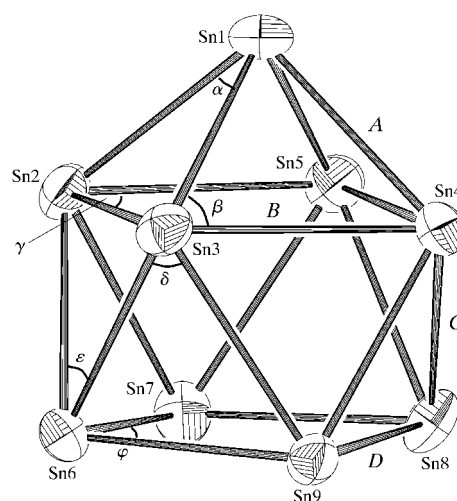


Figure 1

ORTEP (Johnson, 1968) view of the $[Sn_9]^{4-}$ cluster anions (50% probability displacement ellipsoids), with labelling of the bond lengths and angles according to approximate C_{4v} point-group symmetry.

perpendicular to the [100] direction (hexagonal close packing). Thus, the packing differs from that observed for the other A_4M_9 compounds (A/Ge : Cr_3Si ; K/Pb : face-centred cubic).

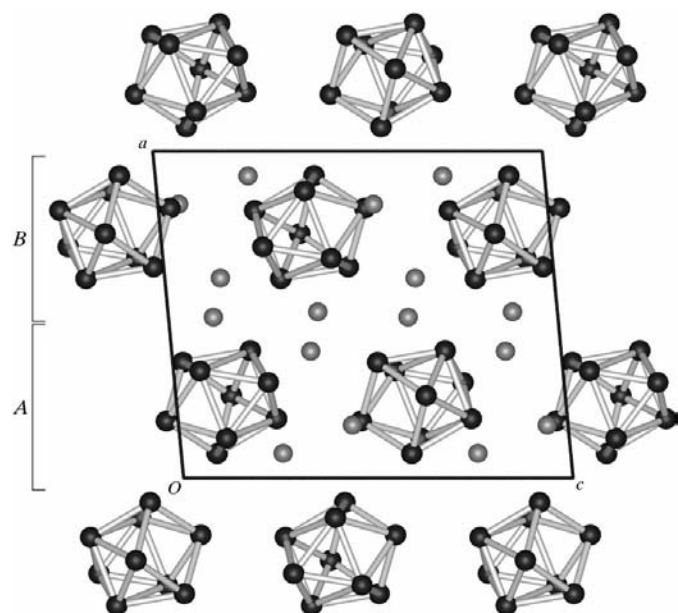


Figure 2
View of the unit cell (projection down [010]) of the crystal structure of K_4Sn_9 (light-gray spheres represent K atoms and dark spheres represent Sn atoms).

Experimental

The crystal used for analysis was taken from a sample with the overall composition KSn_2 . Potassium (460.2 mg, 11.77 mmol; Merck, 99.8%) was reacted with elemental Sn (2539.8 mg, 21.40 mmol; ABCR, 99.9%) in corundum crucibles under an argon atmosphere. The mixtures were heated to 1280 K over a period of 3 h, annealed at that temperature for 2 h and finally cooled to room temperature at a rate of 20 K h^{-1} . The homogeneous samples show silver metallic luster. The very hygroscopic irregular crystals of the title compound were handled in a dry-box under an argon atmosphere and prepared in capillaries filled with dried oil.

Crystal data

K_4Sn_9	$D_x = 4.165 \text{ Mg m}^{-3}$
$M_r = 1224.61$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 980 reflections
$a = 14.238 (2) \text{ \AA}$	$\theta = 2.7\text{--}28.8^\circ$
$b = 8.3554 (13) \text{ \AA}$	$\mu = 12.12 \text{ mm}^{-1}$
$c = 16.487 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 95.261 (3)^\circ$	Irregular, metallic light silver
$V = 1953.2 (5) \text{ \AA}^3$	$0.08 \times 0.06 \times 0.03 \text{ mm}$
$Z = 4$	

Data collection

Bruker AXS CCD diffractometer	3176 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.032$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 28.0^\circ$
$T_{\text{min}} = 0.432$, $T_{\text{max}} = 0.695$	$h = -18 \rightarrow 18$
11 888 measured reflections	$k = -11 \rightarrow 9$
4575 independent reflections	$l = -21 \rightarrow 16$
	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 3.4250P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.97$	$\Delta\rho_{\text{max}} = 1.22 \text{ e \AA}^{-3}$
4575 reflections	$\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$
118 parameters	

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWxtl* (Finger & Kroeker, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1356). Services for accessing these data are described at the back of the journal.

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