Crystal structure of di[potassium(18-crown-6)]dipotassium nonastannide(4–) — diethylenediamine solvate (1:1.5), $[K(C_{12}H_{24}O_6)]_2K_2[Sn_9] \cdot 1.5C_2N_2H_8$

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Abstract

$C_{27}H_{60}K_4N_3O_{12}Sn_9$, monoclinic, $P12_1/n1$ (No. 14), $a = 10.410(2) \text{ \AA}$, $b = 25.659(5) \text{ \AA}$, $c = 20.636(4) \text{ \AA}$, $\beta = 102.56(3)^\circ$, $V = 5380.2 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.030$, $wR_{\text{ref}}(F^2) = 0.072$, $T = 150 \text{ K}$.

Source of material

All experiments were carried out under argon atmosphere using a glove-box or a Schlenk line. Ethylenediamine (en) and toluene were dried over CaH_2 and freshly distilled. The elements K and Sn were sealed in a niobium ampoule in the molar ratio 4:9 and the ampoule was heated to 873 K for 5 h. To 0.20 g of the resulting alloy 4 ml of ethylenediamine was added and then the mixture was sonicated for 5 min and filtered. The filtrate was layered with a solution of 0.20 g of 18-crown-6(1,4,7,10,13,16-hexaoxacyclo-octadecane) in 6 ml of toluene. After one week the product was obtained in form of dark red crystals.

Discussion

During our investigations of the arrangement of Zintl ions by connecting them via alkali metals [1–4] we were able to synthesize the title compound

It consists of two $[K(18\text{-crown-6})]^+$ cations, two K^+ cations, a $[Sn_9]^{4-}$ cluster anion and 1.5 ethylenediamine molecules (figure, top). According to Wade rules a nine-atom cluster can adopt a mono-capped square antiprism with C_{4v} symmetry (*nido* type) or a tricapped trigonal prism with D_{3h} symmetry (*closo* type) [5]. The $[Sn_9]^{4-}$ cluster anion has 22 skeletal electrons and can be described as a mono-capped square antiprism as expected from the Wade rules (figure, middle). The ratio of the diagonal lengths of the open square is $d(Sn1-Sn2)/d(Sn3-Sn4) = 1.02$. The Sn—Sn bond length range from 2.927(1) Å to 3.264(1) Å, and thus only slightly distorted from C_{4v} symmetry. This values are comparable with those one in other nonastannide anions [1–4, 6–8]. The $[Sn_9]$ cluster anions are connected via the K^+ cations to a two-dimensional intermetallic slab (figure, bottom). The $[K(18\text{-crown-6})]^+$ cations are also bound to the $[Sn_9]$ cluster anions. Therefore the intermetallic slab has the composition ${}^2[K_4Sn_9]$. The structure is isotypic to that of $[Rb(18\text{-crown-6})]_2Rb_2[Sn_9](en)_{1.5}$ [1].

Table 1. Data collection and handling.

Crystal:	dark red column, size $0.26 \times 0.27 \times 0.34 \text{ mm}$
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	44.60 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{\text{max}}$:	54.2°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	84815, 11805
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 9439
$N(\text{param})_{\text{refined}}$:	496
Programs:	SHELXS-97 [9], SHELXL-97 [10]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1A)	4e	0.2981	0.1596	0.3133	0.055
H(1B)	4e	0.428	0.1504	0.3674	0.055
H(2A)	4e	0.3623	0.0637	0.3787	0.050
H(2B)	4e	0.2616	0.1035	0.3977	0.050
H(3A)	4e	0.0984	0.0366	0.3722	0.053
H(3B)	4e	0.1954	-0.0018	0.3475	0.053
H(4A)	4e	-0.0286	-0.0178	0.2951	0.054
H(4B)	4e	-0.0334	0.0377	0.2622	0.054
H(5A)	4e	-0.0773	-0.0044	0.1542	0.046
H(5B)	4e	-0.0724	-0.0581	0.1915	0.046
H(6A)	4e	0.1102	-0.0822	0.1462	0.051
H(6B)	4e	-0.0183	-0.0740	0.0907	0.051
H(7A)	4e	0.0928	-0.0474	0.0061	0.050
H(7B)	4e	0.2208	-0.0653	0.0568	0.050
H(8A)	4e	0.2734	-0.0052	-0.0192	0.053
H(8B)	4e	0.1822	0.0364	0.0042	0.053
H(9A)	4e	0.3776	0.0895	0.0330	0.056
H(9B)	4e	0.4699	0.0448	0.0177	0.056
H(10A)	4e	0.5717	0.0442	0.1338	0.058
H(10B)	4e	0.5995	0.0951	0.0967	0.058
H(11A)	4e	0.6202	0.1512	0.1933	0.055
H(11B)	4e	0.6185	0.0983	0.2316	0.055
H(12A)	4e	0.5542	0.1703	0.2905	0.056
H(12B)	4e	0.4302	0.1776	0.2321	0.056
H(13A)	4e	-0.4506	0.4589	0.0066	0.037
H(13B)	4e	-0.3356	0.4196	0.0344	0.037
H(14A)	4e	-0.2633	0.5079	0.0474	0.036
H(14B)	4e	-0.3604	0.5169	0.0951	0.036
H(15A)	4e	-0.1876	0.5286	0.1965	0.040
H(15B)	4e	-0.1031	0.534	0.1423	0.040

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(16A)	4e	0.0267	0.4620	0.1917	0.042
H(16B)	4e	0.0392	0.5100	0.2401	0.042
H(17A)	4e	0.1023	0.4520	0.3276	0.041
H(17B)	4e	0.0718	0.4001	0.2863	0.041
H(18A)	4e	0.0449	0.3896	0.3972	0.044
H(18B)	4e	-0.0694	0.4309	0.3825	0.044
H(19A)	4e	-0.2356	0.3776	0.3959	0.039
H(19B)	4e	-0.1361	0.3319	0.4198	0.039
H(20A)	4e	-0.2505	0.2813	0.3295	0.040
H(20B)	4e	-0.3381	0.2947	0.3804	0.040
H(21A)	4e	-0.5295	0.2858	0.3034	0.044
H(21B)	4e	-0.4579	0.2718	0.2459	0.044
H(22A)	4e	-0.6714	0.3096	0.2071	0.048
H(22B)	4e	-0.6147	0.3619	0.2415	0.048
H(23A)	4e	-0.6555	0.4048	0.1401	0.052
H(23B)	4e	-0.7073	0.3548	0.0986	0.052
H(24A)	4e	-0.5255	0.3622	0.0462	0.049
H(24B)	4e	-0.6259	0.4087	0.0291	0.049
H(25A)	4e	-0.0010	0.4825	0.0646	0.045
H(25B)	4e	-0.0928	0.4601	0.0001	0.045
H(26A)	4e	-0.1644	0.1421	0.4295	0.082
H(26B)	4e	-0.2447	0.1704	0.3667	0.082
H(27A)	4e	-0.1539	0.1157	0.3261	0.168
H(27B)	4e	-0.0308	0.1148	0.3842	0.168
H(1C)	4e	0.1518	0.4445	-0.0102	0.067
H(1D)	4e	0.0942	0.4071	0.0309	0.067
H(2C)	4e	-0.0479	0.2093	0.4592	0.054
H(2D)	4e	-0.1688	0.2352	0.4257	0.054
H(3C)	4e	-0.0573	0.1548	0.2710	0.050
H(3D)	4e	0.0619	0.1430	0.3196	0.050

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Sn(1)	4e	-0.13270(3)	0.21703(1)	-0.06521(2)	0.0244(2)	0.0421(2)	0.0220(2)	-0.0001(1)	0.0034(1)	-0.0038(1)
Sn(2)	4e	-0.09448(3)	0.13795(1)	0.11739(2)	0.0229(2)	0.0180(1)	0.0367(2)	0.0004(1)	0.0068(1)	0.0030(1)
Sn(3)	4e	0.08440(3)	0.16447(1)	0.02771(2)	0.0307(2)	0.0224(1)	0.0277(2)	0.0063(1)	0.0092(1)	-0.0024(1)
Sn(4)	4e	-0.30870(3)	0.18977(1)	0.02255(2)	0.0208(2)	0.0263(2)	0.0284(2)	-0.0053(1)	0.0021(1)	-0.0006(1)
Sn(5)	4e	-0.19510(3)	0.24092(1)	0.15213(2)	0.0219(2)	0.0222(1)	0.0256(2)	-0.0006(1)	0.0090(1)	-0.0021(1)
Sn(6)	4e	-0.22483(3)	0.30051(1)	0.01533(2)	0.0236(2)	0.0207(1)	0.0357(2)	0.0050(1)	0.0031(1)	0.0039(1)
Sn(7)	4e	0.10970(3)	0.21902(1)	0.15624(2)	0.0194(2)	0.0255(1)	0.0248(2)	0.0002(1)	0.0014(1)	-0.0020(1)
Sn(8)	4e	0.07890(3)	0.28021(1)	0.01505(2)	0.0243(2)	0.0233(1)	0.0330(2)	-0.0046(1)	0.0123(1)	-0.0016(1)
Sn(9)	4e	-0.00857(3)	0.32309(1)	0.13073(2)	0.0252(2)	0.0203(1)	0.0356(2)	-0.0037(1)	0.0100(1)	-0.0080(1)
K(1)	4e	0.0426(1)	0.26606(5)	0.32694(6)	0.0352(6)	0.0374(6)	0.0445(6)	0.0019(5)	0.0031(5)	-0.0062(5)
K(2)	4e	0.4224(1)	0.23068(7)	0.09613(7)	0.0251(6)	0.104(1)	0.0467(7)	0.0061(7)	0.0091(6)	-0.0100(8)
K(3)	4e	0.2210(1)	0.06936(4)	0.17349(5)	0.0251(5)	0.0231(4)	0.0322(5)	-0.0009(4)	0.0039(4)	0.0010(4)
K(4)	4e	-0.2698(1)	0.38034(4)	0.19937(5)	0.0240(5)	0.0234(4)	0.0294(5)	-0.0008(4)	0.0056(4)	-0.0001(4)
O(1)	4e	0.4241(4)	0.1129(1)	0.2839(2)	0.039(2)	0.020(2)	0.045(2)	-0.005(1)	0.003(2)	-0.001(2)
O(2)	4e	0.1967(4)	0.0694(1)	0.3111(2)	0.046(2)	0.029(2)	0.029(2)	0.000(2)	0.003(2)	0.000(1)
O(3)	4e	0.0793(4)	-0.0122(1)	0.2279(2)	0.039(2)	0.027(2)	0.037(2)	-0.007(2)	0.010(2)	-0.001(1)
O(4)	4e	0.1104(4)	-0.0165(1)	0.0958(2)	0.044(2)	0.024(2)	0.034(2)	0.000(2)	0.006(2)	-0.008(1)
O(5)	4e	0.3449(4)	0.0216(2)	0.0713(2)	0.039(2)	0.041(2)	0.038(2)	0.003(2)	0.008(2)	0.011(2)
O(6)	4e	0.4705(4)	0.1059(2)	0.1545(2)	0.024(2)	0.055(2)	0.051(2)	-0.004(2)	0.006(2)	0.010(2)
O(7)	4e	-0.4615(3)	0.4278(1)	0.0932(2)	0.029(2)	0.031(2)	0.036(2)	-0.005(1)	0.003(2)	-0.008(2)
O(8)	4e	-0.2116(3)	0.4703(1)	0.1326(2)	0.029(2)	0.021(1)	0.029(2)	-0.001(1)	-0.002(1)	0.003(1)
O(9)	4e	-0.0698(3)	0.4531(1)	0.2632(2)	0.029(2)	0.030(2)	0.029(2)	-0.004(1)	0.001(1)	0.005(1)
O(10)	4e	-0.1158(3)	0.3639(1)	0.3349(2)	0.036(2)	0.029(2)	0.026(2)	-0.005(1)	0.006(2)	-0.001(1)
O(11)	4e	-0.3859(3)	0.3347(1)	0.2967(2)	0.029(2)	0.028(2)	0.036(2)	-0.004(1)	0.009(2)	-0.001(1)
O(12)	4e	-0.5403(3)	0.3433(1)	0.1640(2)	0.022(2)	0.039(2)	0.039(2)	-0.000(1)	0.002(2)	-0.001(2)
C(1)	4e	0.3629(7)	0.1337(2)	0.3329(3)	0.057(4)	0.030(3)	0.043(3)	0.001(3)	-0.005(3)	-0.012(2)
C(2)	4e	0.2982(6)	0.0905(2)	0.3615(3)	0.053(4)	0.038(3)	0.029(3)	0.011(3)	0.000(2)	-0.004(2)
C(3)	4e	0.1331(7)	0.0263(2)	0.3342(3)	0.065(4)	0.039(3)	0.031(3)	-0.005(3)	0.019(3)	0.004(2)
C(4)	4e	0.0236(6)	0.0086(2)	0.2790(3)	0.051(4)	0.043(3)	0.045(3)	-0.009(3)	0.023(3)	0.001(3)
C(5)	4e	-0.0197(6)	-0.0323(2)	0.1747(3)	0.038(3)	0.029(2)	0.046(3)	-0.010(2)	0.003(2)	0.000(2)
C(6)	4e	0.0463(6)	-0.0566(2)	0.1248(3)	0.050(3)	0.025(2)	0.046(3)	-0.011(2)	-0.004(3)	-0.005(2)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(7)	4e	0.1635(6)	−0.0359(2)	0.0420(3)	0.046(3)	0.039(3)	0.037(3)	0.012(2)	0.003(2)	−0.012(2)
C(8)	4e	0.2392(6)	0.0067(2)	0.0184(3)	0.048(3)	0.055(3)	0.028(3)	0.016(3)	0.006(2)	0.002(2)
C(9)	4e	0.4286(6)	0.0593(2)	0.0515(3)	0.050(4)	0.044(3)	0.054(3)	0.013(3)	0.031(3)	0.017(3)
C(10)	4e	0.5314(6)	0.0750(2)	0.1107(3)	0.035(3)	0.043(3)	0.073(4)	0.006(2)	0.025(3)	0.024(3)
C(11)	4e	0.5638(5)	0.1262(2)	0.2089(3)	0.025(3)	0.044(3)	0.064(4)	−0.008(2)	−0.001(3)	0.024(3)
C(12)	4e	0.4922(6)	0.1523(2)	0.2557(3)	0.037(3)	0.027(2)	0.065(4)	−0.013(2)	−0.012(3)	0.013(3)
C(13)	4e	−0.3903(5)	0.4469(2)	0.0465(2)	0.037(3)	0.026(2)	0.027(2)	0.004(2)	0.002(2)	0.001(2)
C(14)	4e	−0.3065(5)	0.4912(2)	0.0790(2)	0.032(3)	0.027(2)	0.031(2)	0.005(2)	0.004(2)	0.003(2)
C(15)	4e	−0.1348(5)	0.5096(2)	0.1710(3)	0.035(3)	0.024(2)	0.038(3)	−0.008(2)	0.003(2)	0.004(2)
C(16)	4e	−0.0209(5)	0.4838(2)	0.2169(3)	0.030(3)	0.033(3)	0.042(3)	−0.013(2)	0.005(2)	0.003(2)
C(17)	4e	0.0337(5)	0.4273(2)	0.3089(3)	0.032(3)	0.031(2)	0.035(3)	−0.006(2)	−0.004(2)	0.004(2)
C(18)	4e	−0.0244(6)	0.4041(2)	0.3628(3)	0.048(3)	0.030(2)	0.028(2)	−0.005(2)	−0.003(2)	0.002(2)
C(19)	4e	−0.1927(5)	0.3477(2)	0.3813(2)	0.036(3)	0.038(3)	0.025(2)	0.004(2)	0.009(2)	0.004(2)
C(20)	4e	−0.2931(5)	0.3094(2)	0.3481(3)	0.035(3)	0.032(2)	0.034(3)	−0.001(2)	0.011(2)	0.007(2)
C(21)	4e	−0.4909(5)	0.3003(2)	0.2686(3)	0.038(3)	0.038(3)	0.037(3)	−0.016(2)	0.017(2)	−0.004(2)
C(22)	4e	−0.5922(5)	0.3304(2)	0.2206(3)	0.032(3)	0.050(3)	0.043(3)	−0.014(2)	0.016(2)	−0.013(3)
C(23)	4e	−0.6291(5)	0.3747(2)	0.1177(3)	0.022(3)	0.033(3)	0.067(4)	−0.001(2)	−0.005(3)	−0.004(3)
C(24)	4e	−0.5630(6)	0.3919(2)	0.0646(3)	0.034(3)	0.029(2)	0.049(3)	−0.003(2)	−0.013(2)	−0.001(2)
C(25)	4e	−0.0067(6)	0.4750(2)	0.0179(3)	0.040(3)	0.033(3)	0.041(3)	−0.001(2)	0.012(2)	0.002(2)
C(26)	4e	−0.1565(8)	0.1644(3)	0.3926(4)	0.074(5)	0.073(5)	0.066(4)	−0.045(4)	0.036(4)	−0.018(4)
C(27)	4e	−0.090(1)	0.1379(4)	0.3545(7)	0.19(1)	0.080(6)	0.21(1)	−0.090(7)	0.17(1)	−0.096(8)
N(1)	4e	0.0934(5)	0.4370(2)	0.0121(3)	0.050(3)	0.036(3)	0.090(4)	0.007(2)	0.031(3)	0.021(3)
N(2)	4e	−0.1029(5)	0.2144(2)	0.4196(2)	0.042(3)	0.050(3)	0.040(3)	0.005(2)	0.003(2)	−0.006(2)
N(3)	4e	−0.0149(5)	0.1604(2)	0.3133(2)	0.047(3)	0.043(3)	0.037(2)	0.004(2)	0.012(2)	0.007(2)

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