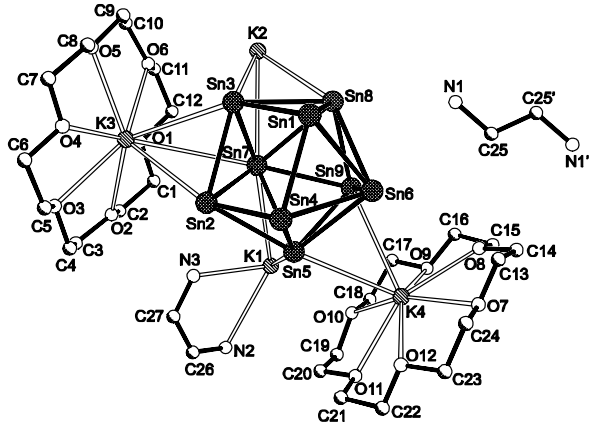
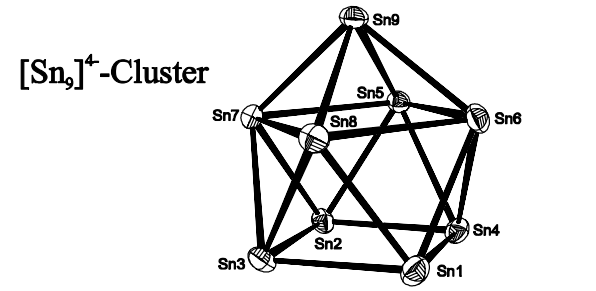
Crystal structure of di[potassium(18-crown-6)]dipotassium nonastannide(4–)—diethylenediamine solvate (1:1.5), $[K(C_{12}H_{24}O_6)]_2K_2[Sn_9] \cdot 1.5C_2N_2H_8$

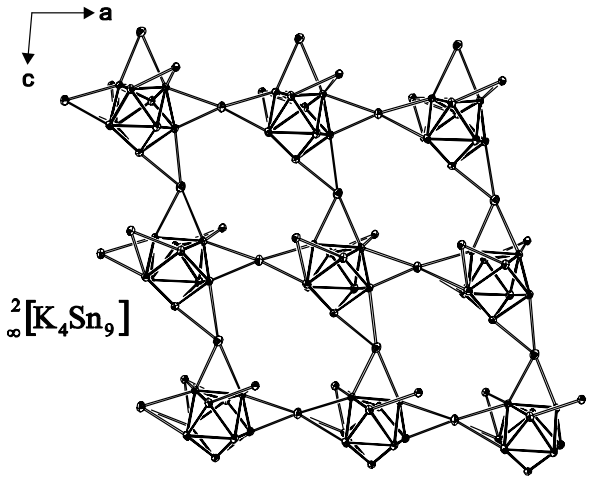
R. Hauptmann and T. F. Fässler*

Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Petersenstr. 18, D-64287 Darmstadt, Germany

Received August 12, 2003, accepted and available on-line November 6, 2003; CCDC-No. 1267/1135







Abstract

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

* Correspondence author (e-mail: faessler@ac.chemie.tu-darmstadt.de)

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-hexaoxacyclooctadecane) 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 $^2_\infty[K_4Sn_9]$. 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 × 0.27 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	44.60 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	54.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	84815, 11805
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 9439
$N(param)_{refined}$:	496
Programs:	SHELXS-97 [9], SHELXL-97 [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

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

Table 2. Continued.

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

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	–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)	4*e*	–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)

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SPP 1072).

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