Crystal structure of di[potassium(diaza-18-crown-6)]dicaesium nonastannide(4–) diethylenediamine, $[K(C_{12}H_{26}N_2O_4)]_2Cs_2[Sn_9] \cdot 2C_2N_2H_8$, *a polyanion* $^2_\infty[KCs_2Sn_9]^-$ *with low-dimensional arrangement of* $[Sn_9]$ *clusters*

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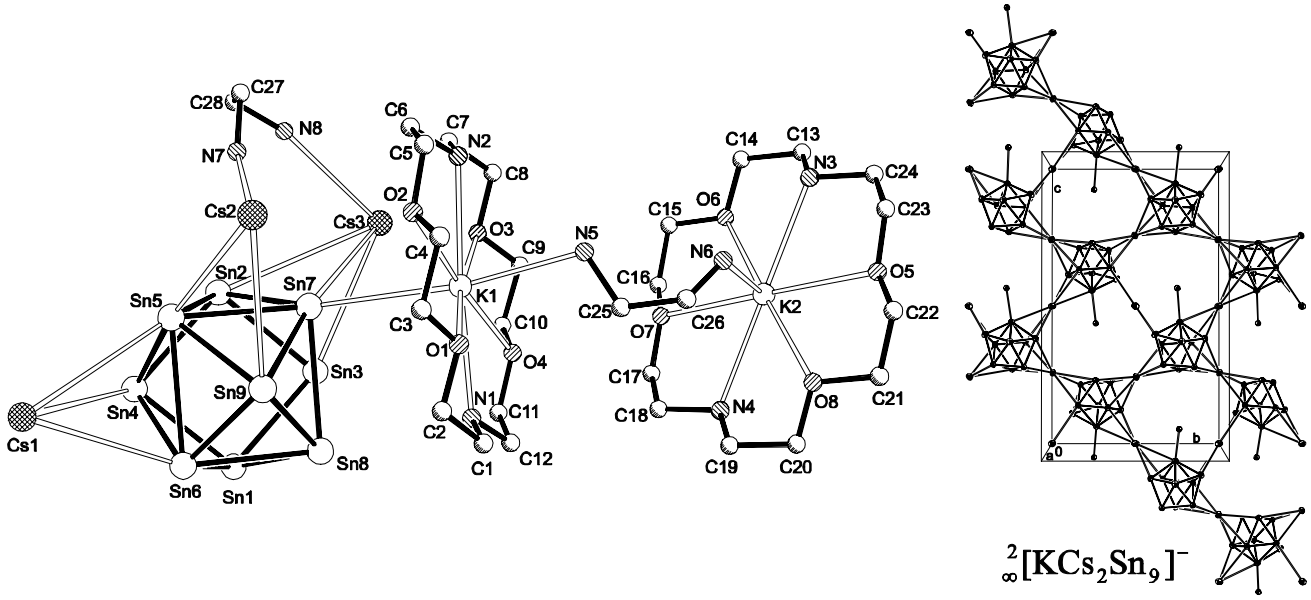

Abstract

$C_{28}H_{68}Cs_2K_2N_8O_8Sn_9$, monoclinic, $P12_1/c1$ (No. 14), $a = 13.897(3)$ Å, $b = 16.091(3)$ Å, $c = 26.432(5)$ Å, $\beta = 91.03(3)°$, $V = 5909.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.050$, $wR_{ref}(F^2) = 0.127$, $T = 153$ 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. $K_2Cs_2Sn_9$ was synthesized by reaction of the elements at 873 K in a sealed niobium ampoule. To 0.20 g of $K_2Cs_2Sn_9$ 4 ml of ethylenediamine was added and the mixture was sonicated for 5 min. The resulting dark red solution was filtered. The filtrate was layered with a solution of 0.10 g of diaza-18-crown-6 in 6 ml of toluene. After one week the product was obtained in form of dark red crystals.

Discussion

The extraction of ternary Zintl phases of the composition $A_nA'_mE_9$ (A and A' = alkali metal, E = Ge, Sn or Pb) is a way to a low dimensional arrangement of the Zintl ions [1,2]. The title compound **I** was synthesized by the extraction of $K_2Cs_2Sn_9$ with ethylenediamine followed by the addition of diaza-18-crown-6. There are two $[K(diaza\text{-}18\text{-}crown\text{-}6)]^+$ and two Cs^+ cations per nonastannide anion, which clearly indicates a charge allocation of 4– for the polyanion. The Sn—Sn bond length occur in the range 2.947(1) Å – 3.274(1) Å with a mean value of 3.012 Å. This values are comparable with those one in other nonastannide anions [1-4]. According to the 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 of **I** has 22 skeletal electrons and as expected from the Wade rules a *nido* structure. The structure of the cluster is comparable to those of other $[Sn_9]^{4-}$ anions [5]. The $[Sn_9]^{4-}$ clusters are connected via the Cs atoms to a two dimensional layer. Each Cs atom is bound to two cluster anions. In contrast to $[Rb(18\text{-}crown\text{-}6)]_2Rb_2[Sn_9](en)_{1.5}$ [2], which contains a comparable slab $^2_\infty[Rb_4Sn_9]$, Cs1 in **I** caps the open rectangle of one cluster anion, whereas Cs2 and Cs3 show comparable η^2 and η^3 coordination as the Rb atoms. The Cs—Sn distances range from 3.822(1) Å to 4.411(1) Å. The shortest not considered Cs···Sn distance is longer than 5 Å. Both K atoms are complexed by diaza-18-crown-6. Whereas K1 is bound to the $[Sn_9]$ cluster, K2 shows no bonding interactions to the cluster anions. The K1—Sn7 bond length is 3.704(2) Å. The distances to the other Sn atoms are longer than 5 Å. The shortest distance of K2 to a Sn atom is the one to Sn1 and longer than 4.9 Å. Therefore, the intermetallic layer has the composition $^2_\infty[KCs_2Sn_9]^-$. The $[K(diaza\text{-}18\text{-}crown\text{-}6)]$ units separate the intermetallic layers. The en molecules are bound to the alkali metals via the N atoms. One en molecule bridges via N5 and N6 the atoms K1 and K2, the second en molecule bridges Cs2 and Cs3 by contacts with N7 and N8, respectively.

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Table 1. Data collection and handling.

Crystal:	dark red column, size 0.19 × 0.22 × 0.42 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	51.33 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, ω/φ
$2\theta_{max}$:	54.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	46371, 12937
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 10715
$N(param)_{refined}$:	517
Programs:	SHELXS-97 [6] SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(1C)	4*e*	0.3861	0.7275	0.4751	0.039
H(2C)	4*e*	0.0860	0.7531	0.6598	0.040
H(3C)	4*e*	0.3367	0.9937	0.3474	0.051
H(4C)	4*e*	0.6333	1.0525	0.1661	0.060
H(1A)	4*e*	0.4925	0.6569	0.5488	0.042
H(1B)	4*e*	0.5046	0.6461	0.4903	0.042
H(2A)	4*e*	0.3537	0.5788	0.4859	0.044
H(2B)	4*e*	0.4275	0.5297	0.5203	0.044
H(3A)	4*e*	0.3044	0.4691	0.5676	0.050
H(3B)	4*e*	0.2302	0.5126	0.5307	0.050
H(4A)	4*e*	0.1666	0.4794	0.6132	0.049
H(4B)	4*e*	0.2341	0.5493	0.6354	0.049
H(5A)	4*e*	0.0903	0.6087	0.6619	0.047
H(5B)	4*e*	0.0162	0.5565	0.6295	0.047
H(6A)	4*e*	–0.0227	0.6811	0.5837	0.048
H(6B)	4*e*	–0.0533	0.6841	0.6407	0.048
H(7A)	4*e*	–0.0361	0.8395	0.6418	0.049
H(7B)	4*e*	–0.0117	0.8341	0.5840	0.049
H(8A)	4*e*	0.0506	0.9558	0.6266	0.047
H(8B)	4*e*	0.1231	0.8963	0.6552	0.047
H(9A)	4*e*	0.2611	0.9554	0.6171	0.049
H(9B)	4*e*	0.1948	1.0214	0.5897	0.049
H(10A)	4*e*	0.2445	0.9608	0.5112	0.054
H(10B)	4*e*	0.3248	1.0117	0.5402	0.054
H(11A)	4*e*	0.4481	0.9305	0.5037	0.043
H(11B)	4*e*	0.3698	0.8802	0.4730	0.043
H(12A)	4*e*	0.5134	0.8014	0.4837	0.045
H(12B)	4*e*	0.5012	0.8051	0.5426	0.045
H(13A)	4*e*	0.3626	1.1614	0.3533	0.064
H(13B)	4*e*	0.2804	1.1115	0.3798	0.064
H(14A)	4*e*	0.2187	1.0728	0.2990	0.065
H(14B)	4*e*	0.2158	1.1696	0.3068	0.065
H(15A)	4*e*	0.2132	1.1767	0.2161	0.057
H(15B)	4*e*	0.2326	1.0813	0.2085	0.057
H(16A)	4*e*	0.2917	1.1624	0.1410	0.068
H(16B)	4*e*	0.3637	1.2052	0.1794	0.068
H(17A)	4*e*	0.5032	1.1512	0.1387	0.069
H(17B)	4*e*	0.4303	1.1197	0.0968	0.069
H(18A)	4*e*	0.4831	0.9820	0.1135	0.071
H(18B)	4*e*	0.5637	1.0384	0.0908	0.071
H(19A)	4*e*	0.6794	0.9356	0.1311	0.067
H(19B)	4*e*	0.5917	0.8890	0.1549	0.067
H(20A)	4*e*	0.7334	0.8661	0.2029	0.066
H(20B)	4*e*	0.7424	0.9621	0.2125	0.066
H(21A)	4*e*	0.7301	0.9473	0.3026	0.072
H(21B)	4*e*	0.7312	0.8506	0.2940	0.072
H(22A)	4*e*	0.5786	0.8425	0.3307	0.071
H(22B)	4*e*	0.6577	0.8745	0.3691	0.071
H(23A)	4*e*	0.5379	0.9412	0.4172	0.064
H(23B)	4*e*	0.4620	0.9035	0.3789	0.064
H(24A)	4*e*	0.4045	1.0233	0.4211	0.056
H(24B)	4*e*	0.4835	1.0757	0.3939	0.056
H(5C)	4*e*	0.2930	0.8069	0.6775	0.061
H(5D)	4*e*	0.2895	0.7167	0.6829	0.061
H(6C)	4*e*	0.4733	0.7829	0.7758	0.068
H(6D)	4*e*	0.3871	0.8062	0.7484	0.068
H(25A)	4*e*	0.4373	0.8070	0.6465	0.066
H(25B)	4*e*	0.4314	0.7114	0.6367	0.066
H(26A)	4*e*	0.4514	0.6856	0.7225	0.064
H(26B)	4*e*	0.5382	0.7373	0.7021	0.064
H(7C)	4*e*	–0.1053	0.7032	0.4899	0.074
H(7D)	4*e*	–0.1691	0.6555	0.4585	0.074
H(8C)	4*e*	–0.1467	0.8051	0.5183	0.254
H(8D)	4*e*	–0.2152	0.8665	0.5298	0.254
H(27A)	4*e*	–0.2109	0.7010	0.5523	0.103
H(27B)	4*e*	–0.2814	0.6557	0.5142	0.103
H(28A)	4*e*	–0.2685	0.7825	0.4551	0.282
H(28B)	4*e*	–0.3200	0.8061	0.5057	0.282

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}
Cs(1)	4*e*	0.00098(4)	0.50398(3)	0.24257(2)	0.0519(3)	0.0340(3)	0.0402(3)	–0.0139(2)	0.0062(2)	–0.0084(2)
Cs(2)	2*a*	0	1/2	1/2	0.0405(4)	0.0515(5)	0.0403(4)	–0.0042(3)	–0.0008(3)	–0.0026(4)
Cs(3)	2*c*	0	0	1/2	0.0472(4)	0.0535(5)	0.0343(4)	0.0121(4)	0.0012(3)	–0.0025(3)
K(1)	4*e*	0.2305(1)	0.7448(1)	0.56421(7)	0.0301(8)	0.0282(8)	0.0295(8)	0.0010(6)	0.0034(7)	0.0000(6)
K(2)	4*e*	0.4830(2)	1.0261(2)	0.25639(8)	0.061(1)	0.063(1)	0.033(1)	0.017(1)	–0.0032(9)	0.0022(9)
Sn(1)	4*e*	0.19956(4)	0.84576(3)	0.28322(2)	0.0328(3)	0.0258(2)	0.0287(3)	–0.0018(2)	0.0045(2)	0.0013(2)
Sn(2)	4*e*	–0.04524(4)	0.83561(3)	0.36814(2)	0.0297(3)	0.0302(3)	0.0330(3)	0.0071(2)	0.0013(2)	–0.0022(2)
Sn(3)	4*e*	0.14930(4)	0.91109(3)	0.38417(2)	0.0373(3)	0.0262(3)	0.0364(3)	–0.0051(2)	0.0087(2)	–0.0072(2)
Sn(4)	4*e*	0.00819(4)	0.76132(3)	0.26938(2)	0.0304(3)	0.0338(3)	0.0233(2)	–0.0003(2)	–0.0025(2)	0.0011(2)
Sn(5)	4*e*	–0.01110(4)	0.65627(3)	0.36016(2)	0.0297(3)	0.0263(2)	0.0307(3)	–0.0063(2)	0.0001(2)	0.0017(2)
Sn(6)	4*e*	0.18397(4)	0.66334(3)	0.29165(2)	0.0303(3)	0.0241(2)	0.0319(3)	0.0009(2)	0.0042(2)	–0.0039(2)
Sn(7)	4*e*	0.09291(4)	0.76380(4)	0.44345(2)	0.0352(3)	0.0368(3)	0.0217(2)	–0.0010(2)	–0.0003(2)	–0.0002(2)
Sn(8)	4*e*	0.28714(4)	0.76999(4)	0.37528(2)	0.0243(3)	0.0395(3)	0.0359(3)	–0.0017(2)	–0.0040(2)	–0.0007(2)
Sn(9)	4*e*	0.18285(4)	0.61484(4)	0.39937(2)	0.0354(3)	0.0328(3)	0.0392(3)	0.0070(2)	0.0011(2)	0.0108(2)
O(1)	4*e*	0.3283(4)	0.5886(3)	0.5587(2)	0.042(3)	0.028(3)	0.035(3)	0.001(2)	0.000(3)	–0.005(2)
O(2)	4*e*	0.1292(4)	0.5927(3)	0.5910(2)	0.036(3)	0.032(3)	0.032(3)	–0.001(2)	–0.001(2)	0.001(2)
O(3)	4*e*	0.1476(4)	0.9049(3)	0.5813(2)	0.034(3)	0.029(3)	0.039(3)	0.003(2)	0.004(2)	–0.005(2)
O(4)	4*e*	0.3430(4)	0.8891(3)	0.5453(2)	0.035(3)	0.030(3)	0.035(3)	–0.001(2)	0.003(2)	0.005(2)
O(5)	4*e*	0.5678(5)	0.9616(4)	0.3462(2)	0.048(4)	0.043(4)	0.045(4)	–0.009(3)	–0.010(3)	0.011(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(6)	4*e*	0.3180(4)	1.1329(4)	0.2605(2)	0.033(3)	0.053(4)	0.047(4)	–0.003(3)	–0.006(3)	–0.004(3)
O(7)	4*e*	0.3946(5)	1.0886(4)	0.1656(2)	0.040(3)	0.059(4)	0.036(3)	–0.010(3)	–0.004(3)	0.011(3)
O(8)	4*e*	0.6375(5)	0.9093(4)	0.2505(3)	0.042(4)	0.051(4)	0.058(4)	–0.006(3)	–0.006(3)	–0.004(3)
N(1)	4*e*	0.4060(5)	0.7304(4)	0.5081(2)	0.037(4)	0.039(4)	0.022(3)	0.001(3)	–0.004(3)	–0.001(3)
N(2)	4*e*	0.0654(5)	0.7542(4)	0.6270(3)	0.038(4)	0.033(4)	0.029(3)	0.004(3)	0.004(3)	0.000(3)
N(3)	4*e*	0.3784(6)	1.0373(5)	0.3473(3)	0.049(4)	0.042(4)	0.038(4)	–0.018(3)	–0.004(3)	0.004(3)
N(4)	4*e*	0.5875(6)	1.0120(6)	0.1651(3)	0.048(5)	0.063(5)	0.040(4)	–0.021(4)	0.005(4)	–0.003(4)
C(1)	4*e*	0.4578(6)	0.6537(5)	0.5167(3)	0.032(4)	0.043(5)	0.031(4)	0.006(3)	0.005(3)	0.000(3)
C(2)	4*e*	0.3909(6)	0.5808(5)	0.5173(3)	0.038(4)	0.038(4)	0.035(4)	0.010(4)	0.003(4)	–0.008(4)
C(3)	4*e*	0.2666(6)	0.5191(5)	0.5621(4)	0.041(5)	0.028(4)	0.056(6)	0.002(3)	–0.006(4)	0.003(4)
C(4)	4*e*	0.1986(6)	0.5313(5)	0.6055(4)	0.044(5)	0.022(4)	0.058(6)	–0.004(3)	–0.004(4)	0.013(4)
C(5)	4*e*	0.0588(7)	0.6042(6)	0.6289(3)	0.044(5)	0.045(5)	0.030(4)	–0.011(4)	0.010(4)	0.004(4)
C(6)	4*e*	0.0013(6)	0.6814(6)	0.6184(3)	0.031(4)	0.053(5)	0.038(4)	–0.010(4)	0.005(4)	–0.005(4)
C(7)	4*e*	0.0159(6)	0.8333(6)	0.6180(3)	0.038(5)	0.047(5)	0.038(5)	0.017(4)	0.006(4)	0.006(4)
C(8)	4*e*	0.0852(7)	0.9036(5)	0.6244(3)	0.053(5)	0.034(4)	0.029(4)	0.017(4)	0.002(4)	–0.002(3)
C(9)	4*e*	0.2229(6)	0.9665(5)	0.5867(4)	0.040(5)	0.029(4)	0.053(5)	0.003(3)	–0.009(4)	–0.005(4)
C(10)	4*e*	0.2843(7)	0.9627(5)	0.5417(4)	0.047(5)	0.025(4)	0.062(6)	–0.003(4)	–0.003(4)	0.004(4)
C(11)	4*e*	0.4063(6)	0.8823(5)	0.5046(3)	0.039(4)	0.039(4)	0.030(4)	–0.007(4)	0.001(3)	0.004(3)
C(12)	4*e*	0.4665(6)	0.8038(6)	0.5104(3)	0.028(4)	0.053(5)	0.033(4)	–0.009(4)	0.008(3)	–0.002(4)
C(13)	4*e*	0.3204(8)	1.1135(7)	0.3501(4)	0.048(6)	0.058(6)	0.054(6)	–0.009(5)	0.011(5)	–0.008(5)
C(14)	4*e*	0.2582(7)	1.1221(7)	0.3035(4)	0.041(5)	0.051(6)	0.070(7)	0.002(4)	0.009(5)	–0.002(5)
C(15)	4*e*	0.2632(6)	1.1348(7)	0.2142(4)	0.030(4)	0.054(6)	0.059(6)	0.001(4)	–0.011(4)	0.002(5)
C(16)	4*e*	0.3289(8)	1.1542(7)	0.1720(4)	0.056(6)	0.057(6)	0.057(6)	–0.005(5)	–0.022(5)	0.009(5)
C(17)	4*e*	0.4629(8)	1.1048(8)	0.1282(4)	0.061(7)	0.071(7)	0.041(5)	–0.028(6)	–0.010(5)	0.017(5)
C(18)	4*e*	0.5242(8)	1.0297(8)	0.1202(4)	0.056(6)	0.091(9)	0.032(5)	–0.035(6)	0.006(4)	0.000(5)
C(19)	4*e*	0.6379(8)	0.9336(7)	0.1601(4)	0.054(6)	0.055(6)	0.060(6)	–0.015(5)	0.022(5)	–0.014(5)
C(20)	4*e*	0.6970(8)	0.9170(6)	0.2072(4)	0.047(6)	0.039(5)	0.080(8)	–0.004(4)	0.003(5)	–0.008(5)
C(21)	4*e*	0.6898(8)	0.8990(7)	0.2963(5)	0.052(6)	0.055(6)	0.072(7)	0.005(5)	–0.013(6)	–0.006(6)
C(22)	4*e*	0.6220(9)	0.8882(7)	0.3384(5)	0.065(7)	0.045(6)	0.066(7)	0.005(5)	–0.016(6)	0.006(5)
C(23)	4*e*	0.5028(7)	0.9513(7)	0.3858(4)	0.054(6)	0.065(7)	0.041(5)	–0.029(5)	–0.014(4)	0.017(5)
C(24)	4*e*	0.4422(7)	1.0273(7)	0.3907(3)	0.050(5)	0.062(6)	0.028(4)	–0.021(5)	–0.002(4)	0.001(4)
N(5)	4*e*	0.3109(6)	0.7585(6)	0.6634(3)	0.039(4)	0.078(6)	0.035(4)	–0.008(4)	0.001(3)	0.003(4)
N(6)	4*e*	0.4516(6)	0.8035(6)	0.7461(3)	0.036(4)	0.080(7)	0.054(5)	–0.007(4)	–0.007(4)	–0.012(5)
C(25)	4*e*	0.4150(7)	0.7548(8)	0.6605(4)	0.042(5)	0.083(8)	0.039(5)	–0.003(5)	0.006(4)	–0.004(5)
C(26)	4*e*	0.4699(8)	0.7391(7)	0.7089(4)	0.042(5)	0.062(7)	0.056(6)	0.002(5)	0.004(5)	–0.002(5)
N(7)	4*e*	–0.1463(7)	0.6600(6)	0.4905(4)	0.069(6)	0.058(6)	0.058(6)	–0.017(5)	0.015(5)	0.009(4)
N(8)	4*e*	–0.185(2)	0.844(1)	0.5035(8)	0.35(4)	0.16(2)	0.13(2)	0.16(2)	0.04(2)	–0.00(1)
C(27)	4*e*	–0.2276(9)	0.694(1)	0.5167(6)	0.056(7)	0.12(1)	0.085(9)	–0.027(8)	0.024(7)	–0.039(9)
C(28)	4*e*	–0.260(1)	0.787(1)	0.492(2)	0.050(9)	0.11(2)	0.55(6)	–0.02(1)	0.11(2)	–0.16(3)

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