Crystal structure of di[K(18-crown-6)]dirubidium nonagermanide(4–) diethylenediamine, $[K(C_{12}H_{26}N_2O_4)]_2Rb_2[Ge_9] \cdot 2C_2N_2H_8$

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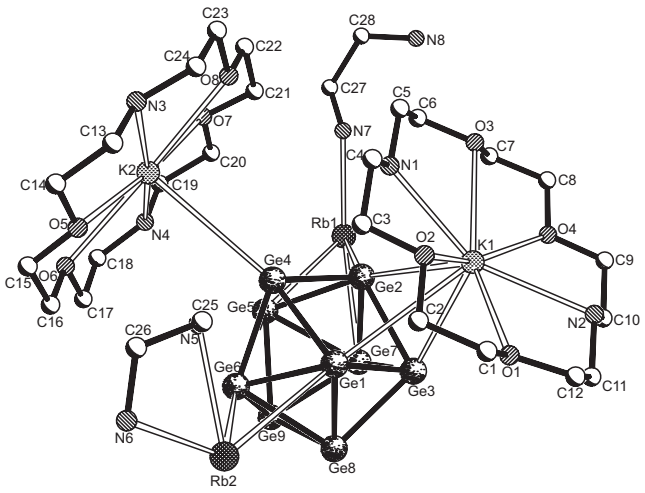
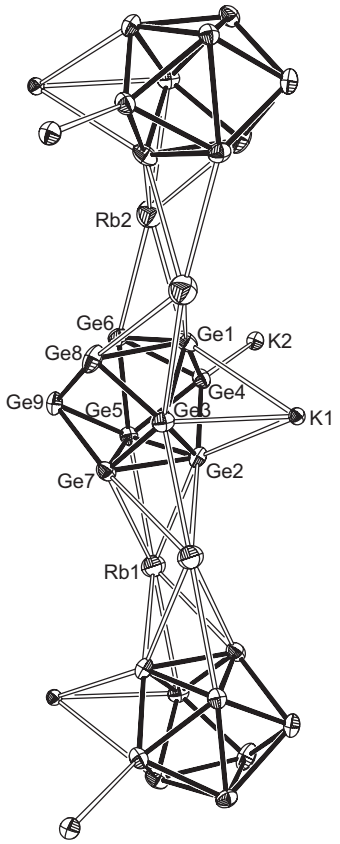


$^1_\infty[K_2Rb_2Ge_9]$



Abstract

$C_{28}H_{68}Ge_9K_2N_8O_8Rb_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 16.864(3)$ Å, $b = 12.091(2)$ Å, $c = 26.466(5)$ Å, $\beta = 97.28(3)°$, $V = 5353.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.058$, $wR_{ref}(F^2) = 0.176$, $T = 153$ 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. The elements K, Rb and Ge were sealed in a niobium ampoule in the molar ratio 2:2:9 and the ampoule was heated to 1013 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 0.10 g of diaza-18-crown-6 in 6 ml of toluene. After one week the product was obtained in form of orange crystals.

Discussion

The extraction of a ternary alloy with formal composition $K_2Rb_2Ge_9$ with ethylenediamine followed by the addition of diaza-18-crown-6 leads the title compound **I**. There are two $[K(\text{diaza-18-crown-6})]^+$ and two Rb^+ cations per nonagermanide anion, which clearly indicates a charge allocation of –4 for the polyanion. The Ge—Ge bond length range from 2.556(1) Å to 2.870(1) Å, giving an average of 2.616 Å. This values are comparable with those one in other nonagermanide anions [1-3].

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) [4]. The structure of the cluster of **I** is best described as a C_{2v} symmetric tricapped trigonal prism with two elongated prism heights (d(Ge1—Ge2) = 3.262(2) Å, d(Ge5—Ge6) = 2.870(1) Å, d(Ge7—Ge8) = 3.144(2) Å) and is analogous to the structure of the $[Ge_9]^{4-}$ anion from $[K(\text{diaza-18-crown-6})]K_3[Ge_9](en)_2$ [1].

The $[Ge_9]$ clusters are connected via the Rb atoms to a infinite chain of the composition $^1_\infty[K_2Rb_2Ge_9]$. Rb1 is bound to two $[Ge_9]$ clusters via the atoms of a triangular face of the cluster, whereas Rb2 is bound to one cluster via a triangular face and to another one via the Ge atoms of a cluster edge. The Rb—Ge distances occur in the range 3.441(2) Å – 3.876(2) Å. The K atoms, which are complexed by diaza-18-crown-6, are also bound to the $[Ge_9]$ cluster, but do not bridge two clusters. The K—Ge distances range from 3.479(2) Å to 3.815(2) Å. The $[K(\text{diaza-18-crown-6})]$ units separate the $^1_\infty[K_2Rb_2Ge_9]$ chains.

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Table 1. Data collection and handling.

Crystal:	orange column, size 0.21 × 0.23 × 0.48 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	69.87 cm^{-1}
Diffractometer, scan mode:	Stoe IPSD II, φ
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	75620, 10529
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7715
$N(param)_{refined}$:	514
Programs:	SHELXS-97 [5] SHELXL-97 [6]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(91)	4*e*	0.2886	0.4097	0.1674	0.039
H(92)	4*e*	0.2529	0.0011	0.0153	0.035
H(93)	4*e*	0.2005	0.6924	0.3394	0.039
H(94)	4*e*	0.3257	0.8468	0.1325	0.032
H(95A)	4*e*	0.0898	0.6014	0.1428	0.048
H(95B)	4*e*	0.0526	0.7059	0.1560	0.048
H(96A)	4*e*	–0.1323	0.7739	0.1323	0.059
H(96B)	4*e*	–0.1756	0.6702	0.1224	0.059
H(97A)	4*e*	0.5530	0.5958	0.1531	0.093
H(97B)	4*e*	0.5946	0.5042	0.1340	0.093
H(98A)	4*e*	0.7637	0.4233	0.1689	0.073
H(98B)	4*e*	0.6805	0.3853	0.1585	0.073
H(1A)	4*e*	0.0451	0.1032	0.0818	0.038
H(1B)	4*e*	–0.0084	0.1770	0.0422	0.038
H(2A)	4*e*	0.0577	0.3366	0.0799	0.039
H(2B)	4*e*	0.0101	0.2734	0.1184	0.039
H(3A)	4*e*	0.0997	0.3478	0.1883	0.055
H(3B)	4*e*	0.1456	0.4109	0.1489	0.055
H(4A)	4*e*	0.2262	0.3706	0.2291	0.052
H(4B)	4*e*	0.2213	0.2454	0.2133	0.052
H(5A)	4*e*	0.3645	0.2396	0.2157	0.045
H(5B)	4*e*	0.3713	0.3651	0.2306	0.045
H(6A)	4*e*	0.4293	0.3974	0.1539	0.037
H(6B)	4*e*	0.4833	0.3242	0.1937	0.037

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7A)	4*e*	0.5399	0.2523	0.1214	0.040
H(7B)	4*e*	0.4787	0.3198	0.0836	0.040
H(8A)	4*e*	0.5261	0.1599	0.0456	0.036
H(8B)	4*e*	0.4842	0.0875	0.0838	0.036
H(9A)	4*e*	0.3954	0.0038	0.0179	0.038
H(9B)	4*e*	0.4349	0.0686	–0.0239	0.038
H(10A)	4*e*	0.3103	0.1562	–0.0476	0.042
H(10B)	4*e*	0.3100	0.0292	–0.0595	0.042
H(11A)	4*e*	0.1678	0.1510	–0.0497	0.044
H(11B)	4*e*	0.1624	0.0226	–0.0578	0.044
H(12A)	4*e*	0.0527	0.0721	–0.0234	0.041
H(12B)	4*e*	0.1080	0.0095	0.0197	0.041
H(13A)	4*e*	0.0755	0.6387	0.3313	0.050
H(13B)	4*e*	0.0785	0.6098	0.2739	0.050
H(14A)	4*e*	0.0122	0.7773	0.2843	0.053
H(14B)	4*e*	0.0926	0.8264	0.3118	0.053
H(15A)	4*e*	0.0852	0.9624	0.2476	0.053
H(15B)	4*e*	0.0084	0.9093	0.2175	0.053
H(16A)	4*e*	0.0805	0.8827	0.1473	0.046
H(16B)	4*e*	0.0707	1.0085	0.1602	0.046
H(17A)	4*e*	0.1880	1.0563	0.1238	0.038
H(17B)	4*e*	0.1964	0.9317	0.1083	0.038
H(18A)	4*e*	0.3217	1.0202	0.1165	0.040
H(18B)	4*e*	0.3135	1.0475	0.1737	0.040
H(19A)	4*e*	0.4360	0.9332	0.2035	0.037
H(19B)	4*e*	0.4441	0.9197	0.1454	0.037
H(20A)	4*e*	0.4351	0.7270	0.1544	0.043
H(20B)	4*e*	0.5103	0.7753	0.1884	0.043
H(21A)	4*e*	0.4994	0.6077	0.2362	0.043
H(21B)	4*e*	0.4158	0.5754	0.2067	0.043
H(22A)	4*e*	0.4367	0.5044	0.2914	0.053
H(22B)	4*e*	0.4364	0.6267	0.3114	0.053
H(23A)	4*e*	0.3262	0.5856	0.3545	0.059
H(23B)	4*e*	0.3237	0.4631	0.3341	0.059
H(24A)	4*e*	0.1939	0.4952	0.2907	0.053
H(24B)	4*e*	0.1946	0.5119	0.3496	0.053
H(25A)	4*e*	0.0068	0.5415	0.1948	0.047
H(25B)	4*e*	–0.0392	0.5205	0.1403	0.047
H(26A)	4*e*	–0.1206	0.6119	0.1939	0.060
H(26B)	4*e*	–0.0611	0.7124	0.1980	0.060
H(27A)	4*e*	0.6497	0.6688	0.1885	0.093
H(27B)	4*e*	0.7035	0.6252	0.1486	0.093
H(28A)	4*e*	0.7364	0.5359	0.2298	0.076
H(28B)	4*e*	0.6497	0.4878	0.2257	0.076

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}
Ge(1)	4*e*	0.15833(5)	0.52428(7)	0.03383(4)	0.0322(4)	0.0243(4)	0.0386(5)	–0.0108(3)	0.0149(4)	–0.0062(4)
Ge(2)	4*e*	0.35336(5)	0.52655(7)	0.04874(3)	0.0276(4)	0.0220(4)	0.0280(4)	0.0049(3)	–0.0018(3)	0.0031(3)
Ge(3)	4*e*	0.25396(5)	0.44915(7)	–0.02668(3)	0.0255(4)	0.0172(4)	0.0356(5)	–0.0005(3)	0.0038(3)	–0.0066(3)
Ge(4)	4*e*	0.25533(5)	0.63270(7)	0.09750(3)	0.0286(4)	0.0298(5)	0.0226(4)	–0.0043(3)	0.0052(3)	0.0013(3)
Ge(5)	4*e*	0.33931(5)	0.74489(7)	0.03877(3)	0.0243(4)	0.0194(4)	0.0243(4)	–0.0055(3)	0.0016(3)	–0.0017(3)
Ge(6)	4*e*	0.16777(5)	0.74246(7)	0.02663(3)	0.0243(4)	0.0194(4)	0.0350(5)	0.0042(3)	0.0044(3)	–0.0033(3)
Ge(7)	4*e*	0.34606(5)	0.61275(7)	–0.04124(3)	0.0295(4)	0.0230(4)	0.0285(4)	–0.0002(3)	0.0119(3)	–0.0004(3)
Ge(8)	4*e*	0.15814(6)	0.60920(7)	–0.05589(4)	0.0427(5)	0.0226(5)	0.0345(5)	0.0005(4)	–0.0186(4)	–0.0020(4)
Ge(9)	4*e*	0.25086(5)	0.77867(7)	–0.04734(3)	0.0383(5)	0.0218(4)	0.0262(4)	0.0020(3)	0.0009(4)	0.0066(3)
Rb(1)	4*e*	0.54802(5)	0.65310(8)	0.03437(4)	0.0377(5)	0.0398(5)	0.0567(6)	0.0010(4)	0.0071(4)	0.0031(4)
Rb(2)	4*e*	–0.03523(7)	0.6560(1)	0.03991(5)	0.0572(6)	0.0558(7)	0.0561(6)	–0.0005(5)	0.0042(5)	0.0017(5)
K(1)	4*e*	0.26494(8)	0.2517(1)	0.06956(6)	0.0177(6)	0.0130(7)	0.0176(7)	–0.0001(5)	0.0036(5)	–0.0002(6)
K(2)	4*e*	0.2554(1)	0.7601(2)	0.22926(7)	0.0284(8)	0.0280(9)	0.0312(9)	0.0036(7)	0.0057(7)	0.0058(7)
O(1)	4*e*	0.1049(3)	0.1722(5)	0.0306(2)	0.032(3)	0.024(3)	0.039(3)	–0.002(2)	0.008(3)	0.002(3)
O(2)	4*e*	0.1272(3)	0.2518(5)	0.1320(3)	0.031(3)	0.030(3)	0.042(4)	0.005(2)	0.004(3)	0.003(3)
O(3)	4*e*	0.4291(3)	0.2385(5)	0.1354(2)	0.029(3)	0.023(3)	0.038(3)	–0.002(2)	0.006(2)	0.001(3)
O(4)	4*e*	0.4081(3)	0.1645(4)	0.0326(2)	0.026(3)	0.020(3)	0.032(3)	0.001(2)	0.001(2)	0.000(2)
O(5)	4*e*	0.0938(3)	0.8028(5)	0.2378(2)	0.035(3)	0.037(3)	0.028(3)	0.005(3)	0.011(2)	–0.005(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*	0.1795(3)	0.9515(5)	0.1808(2)	0.035(3)	0.028(3)	0.029(3)	0.005(2)	0.002(2)	0.000(3)
O(7)	4*e*	0.4233(3)	0.7305(5)	0.2279(2)	0.033(3)	0.033(3)	0.032(3)	0.000(2)	–0.002(2)	–0.002(3)
O(8)	4*e*	0.3312(4)	0.5755(5)	0.2796(2)	0.042(3)	0.038(4)	0.029(3)	0.011(3)	0.004(3)	0.003(3)
N(1)	4*e*	0.2878(4)	0.3352(6)	0.1721(3)	0.037(4)	0.023(4)	0.036(4)	–0.002(3)	0.003(3)	–0.004(3)
N(2)	4*e*	0.2488(4)	0.0672(6)	–0.0013(3)	0.034(4)	0.024(4)	0.031(4)	–0.003(3)	0.003(3)	–0.002(3)
N(3)	4*e*	0.1849(4)	0.6534(6)	0.3105(3)	0.041(4)	0.029(4)	0.028(4)	0.000(3)	0.007(3)	0.000(3)
N(4)	4*e*	0.3337(4)	0.8866(5)	0.1619(3)	0.029(3)	0.022(3)	0.027(3)	0.002(3)	–0.001(3)	–0.002(3)
N(5)	4*e*	0.0435(5)	0.6391(7)	0.1414(3)	0.037(4)	0.045(5)	0.039(4)	0.005(3)	0.007(3)	0.002(4)
N(6)	4*e*	–0.1266(5)	0.7005(8)	0.1286(4)	0.039(4)	0.054(6)	0.053(5)	–0.001(4)	–0.005(4)	0.009(4)
N(7)	4*e*	0.5943(7)	0.578(1)	0.1361(4)	0.083(8)	0.083(8)	0.067(7)	0.021(7)	0.013(6)	–0.026(7)
N(8)	4*e*	0.7183(7)	0.4112(9)	0.1826(4)	0.076(7)	0.055(6)	0.049(6)	0.025(5)	–0.002(5)	0.006(5)
C(1)	4*e*	0.0434(4)	0.1718(8)	0.0627(3)	0.018(3)	0.037(5)	0.042(5)	–0.001(3)	0.005(3)	0.016(4)
C(2)	4*e*	0.0548(5)	0.2684(8)	0.0988(3)	0.023(4)	0.041(5)	0.036(5)	0.013(3)	0.011(3)	0.015(4)
C(3)	4*e*	0.1426(6)	0.3419(9)	0.1673(4)	0.047(5)	0.042(6)	0.054(6)	–0.001(4)	0.023(5)	–0.011(5)
C(4)	4*e*	0.2210(6)	0.320(1)	0.2003(4)	0.044(5)	0.053(6)	0.036(5)	–0.002(4)	0.018(4)	–0.011(5)
C(5)	4*e*	0.3643(6)	0.3141(8)	0.2021(3)	0.050(5)	0.031(5)	0.029(4)	0.001(4)	–0.001(4)	–0.004(4)
C(6)	4*e*	0.4329(5)	0.3268(7)	0.1714(3)	0.034(4)	0.026(4)	0.028(4)	–0.005(3)	–0.007(3)	0.002(3)
C(7)	4*e*	0.4871(5)	0.2506(8)	0.1020(4)	0.022(4)	0.038(5)	0.038(5)	0.001(3)	–0.002(3)	0.012(4)
C(8)	4*e*	0.4817(4)	0.1571(7)	0.0655(4)	0.021(4)	0.028(4)	0.043(5)	0.005(3)	0.006(3)	0.008(4)
C(9)	4*e*	0.3936(5)	0.0719(7)	–0.0015(3)	0.033(4)	0.026(4)	0.038(5)	0.000(3)	0.010(4)	–0.007(4)
C(10)	4*e*	0.3146(6)	0.0832(7)	–0.0323(3)	0.055(5)	0.021(4)	0.031(5)	–0.006(4)	0.015(4)	–0.004(4)
C(11)	4*e*	0.1694(5)	0.0805(8)	–0.0322(4)	0.048(5)	0.024(4)	0.035(5)	0.011(4)	–0.005(4)	–0.007(4)
C(12)	4*e*	0.1032(5)	0.0755(7)	–0.0013(4)	0.031(4)	0.020(4)	0.048(5)	–0.003(3)	–0.008(4)	–0.002(4)
C(13)	4*e*	0.0980(5)	0.6608(9)	0.3009(4)	0.040(5)	0.057(6)	0.030(5)	–0.016(4)	0.013(4)	–0.006(4)
C(14)	4*e*	0.0700(6)	0.7739(9)	0.2862(4)	0.042(5)	0.056(6)	0.038(5)	0.002(4)	0.018(4)	–0.004(5)
C(15)	4*e*	0.0664(6)	0.9084(9)	0.2217(4)	0.044(5)	0.040(5)	0.053(6)	0.013(4)	0.020(5)	–0.001(5)
C(16)	4*e*	0.0952(5)	0.9395(8)	0.1726(4)	0.030(4)	0.032(5)	0.051(6)	0.006(4)	–0.003(4)	0.004(4)
C(17)	4*e*	0.2105(5)	0.9854(7)	0.1352(3)	0.041(4)	0.024(4)	0.029(4)	0.004(3)	0.003(4)	0.002(3)
C(18)	4*e*	0.2997(5)	0.9944(7)	0.1465(3)	0.049(5)	0.024(4)	0.028(4)	0.000(4)	0.003(4)	0.003(4)
C(19)	4*e*	0.4208(5)	0.8876(7)	0.1737(3)	0.029(4)	0.037(5)	0.026(4)	–0.007(3)	0.001(3)	–0.004(4)
C(20)	4*e*	0.4523(5)	0.7739(8)	0.1834(4)	0.024(4)	0.046(5)	0.038(5)	0.001(4)	0.007(3)	–0.007(4)
C(21)	4*e*	0.4421(5)	0.6180(8)	0.2351(4)	0.028(4)	0.035(5)	0.043(5)	0.009(4)	–0.004(4)	–0.006(4)
C(22)	4*e*	0.4157(5)	0.5780(9)	0.2837(4)	0.038(5)	0.038(5)	0.051(6)	0.009(4)	–0.013(4)	–0.003(5)
C(23)	4*e*	0.3051(7)	0.5379(9)	0.3265(4)	0.073(7)	0.045(6)	0.032(5)	0.019(5)	0.017(5)	0.013(5)
C(24)	4*e*	0.2142(6)	0.5414(8)	0.3194(4)	0.065(6)	0.032(5)	0.038(5)	0.004(4)	0.017(5)	0.006(4)
C(25)	4*e*	–0.0173(5)	0.5774(9)	0.1638(4)	0.036(5)	0.047(6)	0.035(5)	–0.006(4)	0.002(4)	0.012(4)
C(26)	4*e*	–0.0835(6)	0.653(1)	0.1759(4)	0.040(5)	0.074(8)	0.036(5)	–0.006(5)	0.003(4)	0.014(5)
C(27)	4*e*	0.6612(8)	0.605(1)	0.1686(6)	0.065(8)	0.09(1)	0.077(9)	0.028(7)	–0.002(7)	–0.027(8)
C(28)	4*e*	0.6923(8)	0.508(1)	0.2061(4)	0.085(9)	0.074(9)	0.032(6)	0.014(7)	0.009(6)	0.002(6)

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