Redetermination of the crystal structure of di-(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-κ^8N_2,O_6) potassium – tetrapotassium octadecagermanide – ethylenediamine (1:1:7), $C_{25}H_{64}Ge_9K_3N_9O_6$

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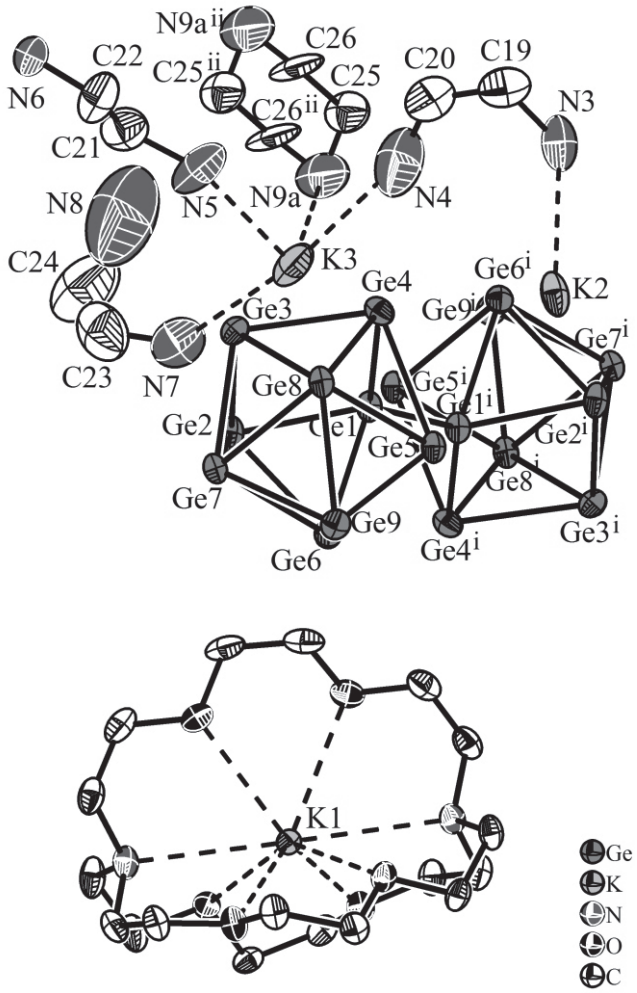

Abstract

$C_{25}H_{64}Ge_9K_3N_9O_6$, triclinic, $P\overline{1}$ (no. 2), a = 9.3766(7) Å, b = 13.540(1) Å, c = 19.507(1) Å, α = 84.527(3)°, β = 81.252(3)°, γ = 80.127(4)°, V = 2405.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.0405, $wR_{ref}(F^2)$ = 0.1050, T = 123 K.

Source of material

All manipulations were carried out under argon atmosphere using a glove-box or a Schlenk line. Ethylenediamine (Alfa-Aesar, 99%) was distilled over CaH_2 and stored in a gas-tight Schlenk tube. Toluene was dried using an MBraun solvent purification system. $K_{12}Ge_{17}$ was prepared from a stoichiometric mixture of the elements at 900°C in niobium ampoules. Cryptand[2.2.2] (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-κ^8N_2,O_6, Acros, 98%) was dried under vacuum for 8 h. 102 mg $K_{12}Ge_{17}$ (41 µmol), 40 mg bis(pentamethylcyclopentadienyl) zinc (102 µmol), and 87 mg cryptand[2.2.2] (230 mmol) were dissolved in 3 ml ethylenediamine in a Schlenk tube. The reaction mixture was stirred at room temperature for 2 d, filtered and layered with 4 ml toluene. After two months block-shaped, very dark red crystals of the title compound were obtained. The same compound, but as a byproduct, resulted from a variation of this procedure: 81 mg $K_{12}Si_8Ge_9$ (60 µmol) and 52 µl bis(trimethylsilyl)-acetylene (240 µmol) were dissolved in 1 ml ethylenediamine and stirred for 3 d. The obtained red solution was filtered and layered with 3 ml toluene containing 151 mg cryptand[2.2.2] (400 µmol). After six weeks many pillar-shaped, very dark red crystals of the title compound were obtained.

Table 1. Data collection and handling.

Crystal:	brown blocks, size 0.21×0.37×0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	58.42 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	41593, 9449
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7877
$N(param)_{refined}$:	478
Programs:	APEX2, SHELX, DIAMOND [8–10]

Experimental details

All H atoms of cryptand and ethylenediamine molecules were included at calculated positions with HFIX and were refined using a riding model with U_{iso} set to 1.2 U_{eq}(C). One ethylenediamine molecule lies on a crystallographic inversion centre and shows orientational disorder. The anisotropic displacement parameters of two C and four N atoms of the solvent molecules had to be restrained using the ISOR option of the SHELX program [8].

Discussion

The crystal structure of the title compound was previously reported two times [1,2], but both the structure determinations differ from ours. Ugrinov and Sevov postulated an amount of eight ethylenediamine molecules per unit cell, which has a volume of 2402.4 Å^3 at 100 K, but did not locate all ethylenediamine atoms on senseful positions [1]. Hauptmann and Fässler found only six solvent molecules in an even larger unit cell of 2426.8 Å^3 (150 K) [2]. In our new structure determination we see seven ethylenediamine molecules per unit cell of a volume of 2405.5(3) Å^3 at 123 K. After obtaining identical results from crystals from different experiments, also concerning the number of solvent molecules in the structure, we propose that all studies mentioned before cover the same compound. The slightly different unit cell

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volumes are a function of temperature, and the probably incorrect finding of six or eight solvent molecules results from other factors like the quality of the investigated single crystals. The unit cell content of the title crystal structure consists of two $[K([2.2.2]crypt)]^+$ complexes, four unsequestered K^+ cations, one $[Ge_9\text{-}Ge_9]^{6-}$ anion located around an inversion center, and seven ethylenediamine molecules. Each $[Ge_9]$ cluster of the $[Ge_9\text{-}Ge_9]^{6-}$ anion can be described as a mono-capped square antiprism, the *nido* type with 22 skeletal electrons according to the Wade rules [3]. Deviating from perfect C_{4v} symmetry, the ratio of the diagonal lengths of the open square, *d*(Ge2–Ge4) /*d*(Ge1–Ge3), is 1.15, resulting in a cluster symmetry close to C_{2v} instead. The Ge–Ge bond lengths in the cluster range from 2.5201(8) Å to 2.8553(8) Å. Two clusters are connected by an *exo* bond of 2.5091(10) Å, which is the shortest Ge–Ge bond in the cluster dimer and is oriented collinear to the shorter diagonal (Ge1–Ge3), as usual for other $[Ge_9\text{-}Ge_9]^{6-}$ anions [4, 5]. The cations K2 and K3 are coordinated directly to the $[Ge_9]$ clusters, which is surprising due to the presence of a cryptand and ethylenediamine both in solution as well as in the crystallized solid, but is found similarly in other $[E_9]$ compounds [6, 7]. K2 coordinates to Ge atoms of different dimeric anions, and by this arrangement K2, K3 and the $[Ge_9\text{-}Ge_9]^{6-}$ anions form one-dimensional $^1{}_\infty\{K_4[Ge_9\text{-}Ge_9]\}^{2-}$ chains along the crystallographic *a* axis. Besides to $[Ge_9]$ clusters, K2 and K3 are bound to bridging as well as to terminal ethylenediamine molecules, respectively, forming extended solvate areas, which alternate with the $^1{}_\infty\{K_4[Ge_9\text{-}Ge_9]\}^{2-}$ chains along *b*, and which together are separated by layers of $[K([2.2.2]crypt)]^+$ cations in the *bc* plane.

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*		–0.1964	0.2739	0.2484	0.035
H(1B)	2*i*		–0.2249	0.3427	0.1791	0.035
H(2A)	2*i*		–0.0308	0.3862	0.2288	0.036
H(2B)	2*i*		0.0591	0.2755	0.2183	0.036
H(3A)	2*i*		0.2558	0.3258	0.1348	0.034
H(3B)	2*i*		0.1824	0.4321	0.1643	0.034
H(4A)	2*i*		0.1497	0.4974	0.0486	0.034
H(4B)	2*i*		0.3192	0.4632	0.0563	0.034
H(5A)	2*i*		0.3451	0.4598	–0.0650	0.031
H(5B)	2*i*		0.1756	0.4674	–0.0729	0.031
H(6A)	2*i*		0.3283	0.3783	–0.1624	0.032
H(6B)	2*i*		0.3926	0.2970	–0.1053	0.032
H(7A)	2*i*		–0.3457	0.1789	0.2027	0.041
H(7B)	2*i*		–0.2764	0.1089	0.1407	0.041
H(8A)	2*i*		–0.4676	0.2331	0.1080	0.039
H(8B)	2*i*		–0.3781	0.3189	0.1209	0.039
H(9A)	2*i*		–0.3587	0.3842	0.0051	0.030
H(9B)	2*i*		–0.4648	0.3078	–0.0061	0.030
H(10A)	2*i*		–0.2937	0.2391	–0.0968	0.029
H(10B)	2*i*		–0.3358	0.3580	–0.1134	0.029
H(11A)	2*i*		–0.1242	0.3444	–0.1885	0.036
H(11B)	2*i*		–0.0450	0.2344	–0.1650	0.036
H(12A)	2*i*		0.1246	0.3456	–0.2109	0.037
H(12B)	2*i*		0.0607	0.4149	–0.1479	0.037
H(13A)	2*i*		–0.1266	0.0880	0.2380	0.038
H(13B)	2*i*		0.0215	0.1337	0.2161	0.038
H(14A)	2*i*		0.0439	–0.0312	0.1799	0.042
H(14B)	2*i*		–0.0814	0.0078	0.1316	0.042
H(15A)	2*i*		0.1055	–0.0482	0.0356	0.046
H(15B)	2*i*		0.2237	–0.0763	0.0887	0.046
H(16A)	2*i*		0.3581	0.0455	0.0259	0.043
H(16B)	2*i*		0.3485	–0.0444	–0.0204	0.043
H(17A)	2*i*		0.3773	0.0551	–0.1255	0.040
H(17B)	2*i*		0.4012	0.1439	–0.0816	0.040

Table 2. continue.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(18A)	2*i*		0.3210	0.2046	–0.1911	0.036
H(18B)	2*i*		0.1718	0.1617	–0.1654	0.036
H(3C)	2*i*		–0.0783	0.7516	0.6554	0.069
H(3D)	2*i*		0.0733	0.7721	0.6449	0.069
H(19A)	2*i*		–0.0982	0.8966	0.5967	0.080
H(19B)	2*i*		–0.0957	0.8192	0.5390	0.080
H(20A)	2*i*		0.0740	0.9188	0.4908	0.133
H(20B)	2*i*		0.1369	0.9182	0.5618	0.133
H(4C)	2*i*		0.1784	0.7805	0.4800	0.135
H(4D)	2*i*		0.2309	0.7738	0.5464	0.135
H(5C)	2*i*		0.3707	0.8494	0.3066	0.102
H(5D)	2*i*		0.3086	0.9219	0.3582	0.102
H(21A)	2*i*		0.4416	1.0370	0.3083	0.079
H(21B)	2*i*		0.5371	0.9567	0.2577	0.079
H(22A)	2*i*		0.2413	1.0229	0.2594	0.081
H(22B)	2*i*		0.3427	0.9484	0.2067	0.081
H(6C)	2*i*		0.3722	1.1445	0.2117	0.061
H(6D)	2*i*		0.3016	1.1065	0.1585	0.061
H(7C)	2*i*		0.8697	0.7321	0.4149	0.098
H(7D)	2*i*		0.8368	0.6815	0.3579	0.098
H(23A)	2*i*		1.0010	0.7505	0.3106	0.123
H(23B)	2*i*		0.8613	0.8224	0.2878	0.123
H(24A)	2*i*		1.0232	0.9150	0.3066	0.183
H(24B)	2*i*		1.0228	0.8654	0.3859	0.183
H(8C)	2*i*		0.7681	0.9640	0.3272	0.398
H(8D)	2*i*		0.7508	0.8980	0.3923	0.398
H(9C)	2*i*	0.5	0.5999	0.8635	0.5705	0.120
H(9D)	2*i*	0.5	0.6387	0.9337	0.5099	0.120
H(25A)	2*i*	0.5	0.4815	1.0067	0.5821	0.072
H(25B)	2*i*	0.5	0.3804	0.9239	0.5786	0.072
H(26A)	2*i*	0.5	0.4037	0.9781	0.4527	0.083
H(26B)	2*i*	0.5	0.2834	1.0386	0.5065	0.083
H(9E)	2*i*	0.5	0.4800	0.9157	0.5605	0.120
H(9F)	2*i*	0.5	0.6329	0.8651	0.5596	0.120

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge(1)	2*i*		0.46063(6)	0.51540(4)	0.44073(3)	0.0180(3)	0.0300(3)	0.0198(3)	–0.0090(2)	–0.0058(2)	–0.0005(2)
Ge(2)	2*i*		0.61875(6)	0.54302(4)	0.32476(3)	0.0191(3)	0.0385(3)	0.0238(3)	–0.0142(2)	–0.0054(2)	0.0052(2)
Ge(3)	2*i*		0.36639(6)	0.63388(4)	0.28979(3)	0.0251(3)	0.0236(3)	0.0246(3)	–0.0057(2)	–0.0082(2)	0.0014(2)
Ge(4)	2*i*		0.21197(6)	0.59391(4)	0.41085(3)	0.0239(3)	0.0332(3)	0.0216(3)	0.0017(2)	–0.0051(2)	–0.0051(2)
Ge(5)	2*i*		0.27828(6)	0.39458(4)	0.43209(3)	0.0181(3)	0.0309(3)	0.0209(3)	–0.0105(2)	–0.0031(2)	0.0005(2)
Ge(6)	2*i*		0.56967(6)	0.35895(4)	0.37089(3)	0.0175(3)	0.0284(3)	0.0249(3)	–0.0011(2)	–0.0042(2)	0.0009(2)
Ge(7)	2*i*		0.48701(6)	0.46139(4)	0.24461(3)	0.0218(3)	0.0304(3)	0.0189(3)	–0.0063(2)	–0.0001(2)	–0.0031(2)
Ge(8)	2*i*		0.19968(5)	0.49636(4)	0.30703(3)	0.0154(3)	0.0336(3)	0.0190(2)	–0.0077(2)	–0.0058(2)	–0.0010(2)
Ge(9)	2*i*		0.36093(7)	0.32004(4)	0.31271(3)	0.0324(3)	0.0260(3)	0.0262(3)	–0.0101(2)	–0.0069(2)	–0.0047(2)
K(1)	2*i*		0.0220(1)	0.24395(8)	0.02201(5)	0.0171(5)	0.0194(5)	0.0214(5)	–0.0054(4)	–0.0037(4)	–0.0010(4)
N(1)	2*i*		–0.1405(4)	0.1995(3)	0.1618(2)	0.015(2)	0.037(3)	0.025(2)	–0.008(2)	–0.004(2)	0.004(2)
N(2)	2*i*		0.1865(5)	0.2853(3)	–0.1189(2)	0.021(2)	0.026(2)	0.024(2)	–0.009(2)	–0.001(2)	–0.003(2)
O(1)	2*i*		0.0416(4)	0.3601(3)	0.1295(2)	0.023(2)	0.036(2)	0.020(2)	–0.011(2)	–0.003(1)	–0.004(2)
O(2)	2*i*		0.2390(4)	0.3709(3)	0.0045(2)	0.029(2)	0.021(2)	0.021(2)	–0.012(2)	–0.002(1)	–0.002(1)

Table 3. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(3)	2*i*		–0.2908(4)	0.2428(3)	0.0374(2)	0.015(2)	0.025(2)	0.026(2)	–0.001(1)	–0.004(1)	0.002(1)
O(4)	2*i*		–0.1382(4)	0.3166(3)	–0.0853(2)	0.019(2)	0.031(2)	0.022(2)	–0.006(2)	–0.006(1)	–0.001(1)
O(5)	2*i*		0.1057(4)	0.0593(3)	0.0980(2)	0.033(2)	0.020(2)	0.033(2)	–0.005(2)	–0.008(2)	0.001(2)
O(6)	2*i*		0.2223(4)	0.0844(3)	–0.0450(2)	0.022(2)	0.028(2)	0.035(2)	–0.000(2)	–0.006(2)	–0.006(2)
C(1)	2*i*		–0.1547(6)	0.2891(4)	0.1996(3)	0.022(3)	0.039(3)	0.024(3)	–0.003(2)	0.002(2)	–0.005(2)
C(2)	2*i*		–0.0135(6)	0.3287(4)	0.1992(3)	0.028(3)	0.040(3)	0.022(3)	–0.011(2)	0.001(2)	–0.005(2)
C(3)	2*i*		0.1836(6)	0.3868(4)	0.1272(3)	0.029(3)	0.035(3)	0.025(3)	–0.015(2)	–0.005(2)	–0.006(2)
C(4)	2*i*		0.2253(6)	0.4387(4)	0.0572(3)	0.033(3)	0.026(3)	0.029(3)	–0.015(2)	0.000(2)	–0.008(2)
C(5)	2*i*		0.2646(6)	0.4205(4)	–0.0630(3)	0.030(3)	0.025(3)	0.026(3)	–0.015(2)	–0.004(2)	0.003(2)
C(6)	2*i*		0.3041(6)	0.3438(4)	–0.1161(3)	0.023(3)	0.036(3)	0.024(3)	–0.015(2)	0.001(2)	–0.002(2)
C(7)	2*i*		–0.2869(6)	0.1777(5)	0.1561(3)	0.021(3)	0.055(4)	0.029(3)	–0.017(3)	–0.004(2)	0.011(3)
C(8)	2*i*		–0.3683(6)	0.2495(5)	0.1067(3)	0.016(3)	0.052(4)	0.028(3)	–0.007(2)	–0.002(2)	0.002(2)
C(9)	2*i*		–0.3612(5)	0.3161(4)	–0.0088(3)	0.015(2)	0.021(3)	0.037(3)	–0.003(2)	–0.008(2)	0.004(2)
C(10)	2*i*		–0.2870(5)	0.3058(4)	–0.0819(3)	0.021(3)	0.026(3)	0.031(3)	–0.009(2)	–0.014(2)	0.003(2)
C(11)	2*i*		–0.0631(6)	0.3060(5)	–0.1547(3)	0.031(3)	0.041(3)	0.019(2)	–0.010(3)	–0.006(2)	0.001(2)
C(12)	2*i*		0.0802(6)	0.3448(4)	–0.1614(3)	0.032(3)	0.037(3)	0.024(3)	–0.011(3)	–0.004(2)	0.006(2)
C(13)	2*i*		–0.0605(6)	0.1125(4)	0.1978(3)	0.025(3)	0.043(3)	0.027(3)	–0.011(2)	–0.007(2)	0.011(2)
C(14)	2*i*		–0.0011(7)	0.0277(4)	0.1521(3)	0.037(3)	0.031(3)	0.038(3)	–0.011(3)	–0.013(3)	0.013(2)
C(15)	2*i*		0.1775(7)	–0.0215(4)	0.0580(3)	0.052(4)	0.017(3)	0.045(3)	0.003(3)	–0.016(3)	–0.003(2)
C(16)	2*i*		0.2908(7)	0.0136(4)	0.0039(3)	0.035(3)	0.028(3)	0.044(3)	0.009(2)	–0.017(3)	–0.011(2)
C(17)	2*i*		0.3270(6)	0.1143(4)	–0.1004(3)	0.025(3)	0.035(3)	0.040(3)	–0.004(2)	0.001(2)	–0.012(3)
C(18)	2*i*		0.2502(6)	0.1907(4)	–0.1497(3)	0.029(3)	0.036(3)	0.026(3)	–0.009(2)	0.002(2)	–0.012(2)
K(2)	2*i*		0.1054(1)	0.5552(1)	0.58243(6)	0.0200(6)	0.074(1)	0.0277(6)	–0.0128(6)	–0.0038(5)	0.0040(6)
N(3)	2*i*		0.0026(6)	0.7547(5)	0.6225(3)	0.040(3)	0.098(5)	0.043(3)	–0.034(3)	–0.010(3)	0.003(3)
C(19)	2*i*		–0.038(1)	0.8401(6)	0.5719(5)	0.065(5)	0.053(5)	0.086(6)	–0.003(4)	–0.026(5)	–0.008(4)
C(20)	2*i*		0.105(2)	0.8746(8)	0.5310(7)	0.135(8)	0.073(6)	0.100(7)	0.016(6)	0.009(6)	0.019(5)
N(4)	2*i*		0.223(1)	0.8155(8)	0.5067(5)	0.092(6)	0.141(7)	0.106(6)	–0.045(5)	–0.023(5)	0.040(5)
K(3)	2*i*		0.5185(2)	0.7588(1)	0.43973(9)	0.095(1)	0.0386(9)	0.055(1)	–0.0199(9)	–0.0167(9)	0.0126(7)
N(5)	2*i*		0.396(1)	0.8927(5)	0.3347(4)	0.158(7)	0.046(4)	0.064(4)	–0.029(4)	–0.051(4)	0.009(3)
C(21)	2*i*		0.438(1)	0.9780(6)	0.2826(5)	0.075(6)	0.057(5)	0.069(5)	–0.012(4)	–0.015(4)	–0.012(4)
C(22)	2*i*		0.341(1)	1.0064(6)	0.2341(4)	0.119(8)	0.053(5)	0.042(4)	–0.039(5)	–0.019(4)	–0.001(3)
N(6)	2*i*		0.3720(6)	1.0909(4)	0.1869(3)	0.043(3)	0.044(3)	0.038(3)	–0.014(2)	–0.012(2)	0.003(2)
N(7)	2*i*		0.8210(9)	0.7429(6)	0.3767(4)	0.093(6)	0.072(5)	0.088(6)	–0.021(4)	–0.027(5)	–0.007(4)
C(23)	2*i*		0.915(1)	0.799(1)	0.3279(5)	0.104(9)	0.14(1)	0.057(6)	0.004(8)	–0.016(6)	–0.011(7)
C(24)	2*i*		0.966(2)	0.881(1)	0.3462(9)	0.25(2)	0.100(9)	0.13(1)	–0.05(1)	–0.07(1)	0.007(8)
N(8)	2*i*		0.806(2)	0.941(2)	0.367(1)	0.27(2)	0.27(2)	0.27(2)	–0.13(1)	–0.02(1)	0.08(1)
N(9A)	2*i*	0.5	0.567(1)	0.8988(7)	0.5319(4)	0.170(9)	0.074(5)	0.044(4)	0.024(6)	–0.026(5)	–0.006(4)
C(25)	2*i*	0.5	0.455(2)	0.961(1)	0.5512(8)	0.08(1)	0.06(1)	0.046(8)	0.002(9)	–0.023(8)	–0.003(7)
C(26)	2*i*	0.5	0.390(2)	1.022(1)	0.4917(9)	0.12(2)	0.016(7)	0.07(1)	0.015(8)	–0.04(1)	–0.005(7)
N(9B)	2*i*	0.5	0.567(1)	0.8988(7)	0.5319(4)	0.170(9)	0.074(5)	0.044(4)	0.024(6)	–0.026(5)	–0.006(4)

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