Crystal structure of di[potassium([2.2.2]crypt)]tetrapotassium octadecagermanide(6–) — ethylenediamine solvate (1:6), $[K(C_{18}H_{36}N_2O_6)]_2K_4(Ge_9)_2 \cdot 6C_2N_2H_8$

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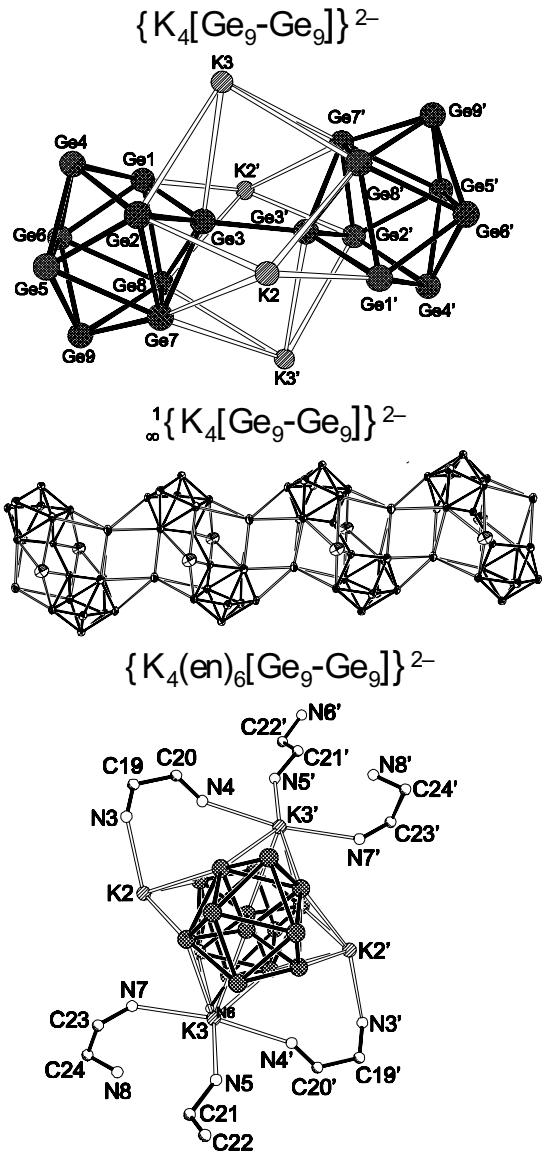

Abstract

$C_{24}H_{60}Ge_9K_3N_8O_6$, triclinic, $P\bar{1}$ (No. 2), a = 9.408(2) Å, b = 13.606(3) Å, c = 19.507(4) Å, α = 84.74(3)°, β = 81.35(3)°, γ = 80.18(3)°, V = 2426.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.064, $wR_{ref}(F^2)$ = 0.192, T = 150 K.

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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 Ge were sealed in a niobium ampoule in the molar ratio 4:9 and the ampoule was heated to 1013 K for 5 h. Ethylenediamine (4 ml) was added to 0.35 g of the resulting alloy and 0.15 g of $Mn[N(SiMe_3)_2]_2$, and then the mixture was sonicated for 5 min and filtered. The filtrate was layered with a solution of 0.20 g of [2.2.2]crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]- hexacosane) in 6 ml of toluene. After one week the product was obtained in form of dark red crystals.

Discussion

Homoatomic nine-atom cluster $[E_9]^{n-}$ of elements of group 14 (E = Ge, Sn, and Pb) in solution are known for a long time and several structures are reported [1,2]. In the case of germanium $[Ge_9]^{3-}$ [3-6] and $[Ge_9]^{4-}$ cluster anions [7-9] are known in solution. Recently dimeric [10,11], trimeric [12] and polymeric anions [13], containing Ge_9 clusters were observed. During our investigations of the reaction behaviour of $[Ge_9]$ clusters in solution towards transition metal compounds [14] we obtained the title compound.

It consists of two $[K([2.2.2]crypt)]^+$ cations, four K^+ cations, a $[Ge_9\text{-}Ge_9]^{6-}$ anion and six ethylenediamine molecules. 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) [1]. The $[Ge_9]$ cluster of the $[Ge_9\text{-}Ge_9]^{6-}$ anion have 22 skeletal electrons and can be described as a mono-capped square antiprism as expected from Wade rules. The ratio of the diagonal lengths of the open square is d(Ge1—Ge2)/d(Ge3—Ge4) = 1.16. This indicates that the cluster is distorted and has only idealized C_{2v} symmetry. The Ge—Ge bond lengths in the cluster range from 2.526(1) Å to 2.856(1) Å. The exo bond is oriented colinear to the shorter diagonal (Ge3—Ge4) and the cluster is compressed along the exo bond. The exo bond length (Ge3—Ge3') is 2.514(1) Å. This value is comparabel to those one in other $[Ge_9\text{-}Ge_9]^{6-}$ anions [10,11]. K2 and K3 connect the clusters of the dimeric anion (figure, top). K2 also coordinates to two Ge atoms of another dimeric anion. This leads to a one-dimensional arrangement of the $[Ge_9\text{-}Ge_9]^{6-}$ cluster anions. K2, K3 and the $[Ge_9\text{-}Ge_9]^{6-}$ anions form a $^1_\infty\{K_4[Ge_9\text{-}Ge_9]\}^{2-}$ chain (figure, middle). The chains are separated by the $[K([2.2.2]crypt)]^+$ cations, which show no bonding interactions to the $[Ge_9\text{-}Ge_9]^{6-}$ cluster anions. The en molecules are bound to K2 and K3, respectively. Whereas one en molecule bridges K2 and K3 by coordination via N3 and N4, respectively,

the two other en molecules are only bound via one N atom to K3 (figure, bottom).

Table 1. Data collection and handling.

Crystal:	dark red column, size 0.20 × 0.21 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	57.88 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω/φ
$2\theta_{max}$:	54.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	38471, 10561
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 9254
$N(param)_{refined}$:	431
Programs:	SHELXS-97 [15], SHELXL-97 [16]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3C)	2*i*	–0.0787	0.7522	0.1534	0.076
H(3D)	2*i*	0.0694	0.7710	0.1457	0.076
H(4C)	2*i*	0.1746	0.7814	–0.0202	0.122
H(4D)	2*i*	0.2256	0.7685	0.0453	0.122
H(5C)	2*i*	0.6877	0.0767	0.1423	0.129
H(5D)	2*i*	0.6300	0.1475	0.1931	0.129
H(6C)	2*i*	0.5518	–0.1173	0.3088	0.060
H(6D)	2*i*	0.6813	–0.1144	0.3436	0.060
H(1A)	2*i*	0.6579	0.1801	0.7015	0.049
H(1B)	2*i*	0.7244	0.1118	0.6406	0.049
H(2A)	2*i*	0.5345	0.2337	0.6072	0.045
H(2B)	2*i*	0.6203	0.3184	0.6202	0.045
H(3A)	2*i*	0.6390	0.3827	0.5044	0.039
H(3B)	2*i*	0.5368	0.3069	0.4938	0.039
H(4A)	2*i*	0.7087	0.2386	0.4032	0.038
H(4B)	2*i*	0.6654	0.3540	0.3859	0.038
H(5A)	2*i*	0.8763	0.3436	0.3124	0.044
H(5B)	2*i*	0.9528	0.2362	0.3353	0.044
H(6A)	2*i*	1.1227	0.3442	0.2900	0.043
H(6B)	2*i*	1.0614	0.4125	0.3515	0.043
H(7A)	2*i*	1.3279	0.3767	0.3381	0.041
H(7B)	2*i*	1.3906	0.2978	0.3941	0.041
H(8A)	2*i*	1.3431	0.4584	0.4349	0.041
H(8B)	2*i*	1.1777	0.4655	0.4270	0.041
H(9A)	2*i*	1.1517	0.4961	0.5485	0.042
H(9B)	2*i*	1.3170	0.4626	0.5565	0.042
H(10A)	2*i*	1.2540	0.3280	0.6330	0.042
H(10B)	2*i*	1.1832	0.4316	0.6623	0.042
H(11A)	2*i*	0.9722	0.3854	0.7279	0.042
H(11B)	2*i*	1.0586	0.2773	0.7171	0.042
H(12A)	2*i*	0.8071	0.2757	0.7477	0.043
H(12B)	2*i*	0.7775	0.3434	0.6804	0.043
H(13A)	2*i*	0.8752	0.0904	0.7366	0.047
H(13B)	2*i*	1.0198	0.1351	0.7152	0.047
H(14A)	2*i*	1.0427	–0.0278	0.6781	0.048
H(14B)	2*i*	0.9202	0.0104	0.6310	0.048
H(15A)	2*i*	1.1065	–0.0454	0.5351	0.053
H(15B)	2*i*	1.2210	–0.0728	0.5876	0.053
H(16A)	2*i*	1.3561	0.0474	0.5250	0.050
H(16B)	2*i*	1.3484	–0.0409	0.4798	0.050
H(17A)	2*i*	1.3760	0.0571	0.3754	0.049
H(17B)	2*i*	1.3974	0.1443	0.4184	0.049
H(18A)	2*i*	1.3196	0.2047	0.3090	0.044
H(18B)	2*i*	1.1737	0.1626	0.3332	0.044
H(19A)	2*i*	–0.0922	0.8963	0.0973	0.091
H(19B)	2*i*	–0.0913	0.8227	0.0397	0.091
H(20A)	2*i*	0.0781	0.9198	–0.0056	0.138
H(20B)	2*i*	0.1417	0.9137	0.0640	0.138
H(21A)	2*i*	0.4632	0.0446	0.2419	0.093
H(21B)	2*i*	0.5528	–0.0347	0.1918	0.093
H(22A)	2*i*	0.7580	–0.0248	0.2408	0.089
H(22B)	2*i*	0.6624	0.0488	0.2931	0.089
N(7)	2*i*	0.179(1)	0.2580(9)	0.1230(6)	0.092(3)
H(7C)	2*i*	0.1618	0.3190	0.1399	0.110
H(7D)	2*i*	0.1319	0.2657	0.0854	0.110
N(8)	2*i*	0.191(5)	0.083(3)	0.150(2)	0.40(3)
H(8C)	2*i*	0.2487	0.1202	0.1601	0.479
H(8D)	2*i*	0.2252	0.0228	0.1383	0.479
C(23)	2*i*	0.089(2)	0.205(1)	0.1712(9)	0.122(5)
H(23A)	2*i*	–0.0012	0.2501	0.1843	0.146
H(23B)	2*i*	0.1360	0.1882	0.2126	0.146
C(24)	2*i*	0.052(3)	0.117(2)	0.151(1)	0.147(7)
H(24A)	2*i*	–0.0108	0.0836	0.1858	0.176
H(24B)	2*i*	0.0186	0.1237	0.1058	0.176

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)	2*i*	0.78786(7)	0.40615(5)	0.08890(3)	0.0271(3)	0.0337(3)	0.0314(3)	0.0030(2)	–0.0054(2)	–0.0060(2)
Ge(2)	2*i*	0.38091(6)	0.45673(5)	0.17495(3)	0.0222(3)	0.0386(3)	0.0322(3)	–0.0130(2)	–0.0069(2)	0.0020(2)
Ge(3)	2*i*	0.53917(6)	0.48421(4)	0.05940(3)	0.0224(3)	0.0305(3)	0.0257(3)	–0.0078(2)	–0.0077(2)	–0.0019(2)
Ge(4)	2*i*	0.63308(7)	0.36607(4)	0.20963(3)	0.0308(3)	0.0253(3)	0.0327(3)	–0.0047(2)	–0.0095(2)	0.0015(2)
Ge(5)	2*i*	0.51204(6)	0.53792(4)	0.25557(3)	0.0263(3)	0.0323(3)	0.0262(3)	–0.0062(2)	–0.0030(2)	–0.0046(2)
Ge(6)	2*i*	0.79905(6)	0.50343(5)	0.19306(3)	0.0201(3)	0.0365(3)	0.0303(3)	–0.0067(2)	–0.0095(2)	–0.0012(2)
Ge(7)	2*i*	0.43036(6)	0.64045(4)	0.12954(3)	0.0223(3)	0.0290(3)	0.0354(3)	–0.0001(2)	–0.0074(2)	–0.0013(2)
Ge(8)	2*i*	0.72121(6)	0.60498(4)	0.06794(3)	0.0233(3)	0.0325(3)	0.0286(3)	–0.0103(2)	–0.0052(2)	0.0006(2)
Ge(9)	2*i*	0.63867(7)	0.67906(5)	0.18785(3)	0.0368(3)	0.0272(3)	0.0367(3)	–0.0111(2)	–0.0093(3)	–0.0059(2)
K(1)	2*i*	1.0217(1)	0.24462(8)	0.52159(6)	0.0220(5)	0.0205(5)	0.0316(5)	–0.0045(4)	–0.0066(4)	–0.0013(4)
K(2)	2*i*	0.1044(2)	0.5559(1)	0.08275(8)	0.0242(6)	0.0657(9)	0.0408(7)	–0.0105(6)	–0.0073(5)	0.0032(6)
K(3)	2*i*	0.4823(3)	0.2415(1)	0.0610(1)	0.096(2)	0.0371(8)	0.063(1)	–0.0218(9)	–0.019(1)	0.0103(7)
O(1)	2*i*	0.7094(4)	0.2436(3)	0.5375(2)	0.022(2)	0.028(2)	0.034(2)	–0.002(2)	–0.009(2)	0.001(2)
O(2)	2*i*	0.8616(4)	0.3170(3)	0.4148(2)	0.027(2)	0.034(2)	0.035(2)	–0.010(2)	–0.012(2)	0.003(2)
O(3)	2*i*	1.2393(5)	0.3709(3)	0.5038(2)	0.036(2)	0.021(2)	0.035(2)	–0.012(2)	–0.004(2)	–0.004(2)
O(4)	2*i*	1.0430(4)	0.3608(3)	0.6293(2)	0.028(2)	0.036(2)	0.033(2)	–0.008(2)	–0.007(2)	–0.006(2)
O(5)	2*i*	1.1047(5)	0.0607(3)	0.5972(2)	0.041(2)	0.021(2)	0.040(2)	–0.003(2)	–0.010(2)	–0.002(2)
O(6)	2*i*	1.2219(5)	0.0849(3)	0.4546(2)	0.030(2)	0.027(2)	0.045(2)	0.001(2)	–0.009(2)	–0.006(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*i*	0.8597(5)	0.2005(4)	0.6608(3)	0.025(2)	0.033(2)	0.033(2)	–0.009(2)	–0.008(2)	0.004(2)
N(2)	2*i*	1.1856(6)	0.2850(4)	0.3808(2)	0.030(2)	0.028(2)	0.033(2)	–0.010(2)	–0.004(2)	–0.003(2)
N(3)	2*i*	0.0019(8)	0.7550(6)	0.1224(4)	0.045(4)	0.085(5)	0.068(4)	–0.031(4)	–0.009(3)	–0.003(4)
N(4)	2*i*	0.220(1)	0.812(1)	0.0076(6)	0.078(7)	0.122(9)	0.107(8)	–0.037(7)	–0.029(6)	0.042(7)
N(5)	2*i*	0.604(2)	0.1061(6)	0.1655(5)	0.22(1)	0.036(4)	0.088(6)	–0.029(6)	–0.093(8)	0.010(4)
N(6)	2*i*	0.6268(7)	–0.0908(5)	0.3124(3)	0.046(3)	0.055(4)	0.054(4)	–0.022(3)	–0.013(3)	0.006(3)
C(1)	2*i*	0.7144(7)	0.1789(6)	0.6556(3)	0.032(3)	0.058(4)	0.035(3)	–0.021(3)	–0.005(2)	0.008(3)
C(2)	2*i*	0.6309(7)	0.2506(5)	0.6062(3)	0.023(3)	0.048(3)	0.042(3)	–0.005(2)	–0.008(2)	–0.002(3)
C(3)	2*i*	0.6376(6)	0.3159(4)	0.4911(3)	0.022(3)	0.021(2)	0.053(4)	–0.002(2)	–0.012(2)	0.006(2)
C(4)	2*i*	0.7133(6)	0.3043(4)	0.4174(3)	0.024(3)	0.026(2)	0.048(3)	–0.003(2)	–0.020(2)	0.002(2)
C(5)	2*i*	0.9360(7)	0.3060(5)	0.3454(3)	0.035(3)	0.044(3)	0.033(3)	–0.008(3)	–0.013(2)	0.000(2)
C(6)	2*i*	1.0798(7)	0.3440(5)	0.3384(3)	0.040(3)	0.038(3)	0.029(3)	–0.011(3)	–0.007(2)	0.007(2)
C(7)	2*i*	1.3043(7)	0.3433(5)	0.3835(3)	0.031(3)	0.039(3)	0.037(3)	–0.018(2)	0.000(2)	–0.004(2)
C(8)	2*i*	1.2646(7)	0.4199(4)	0.4367(3)	0.036(3)	0.027(3)	0.040(3)	–0.012(2)	–0.006(2)	0.000(2)
C(9)	2*i*	1.2253(7)	0.4389(4)	0.5570(3)	0.039(3)	0.026(3)	0.044(3)	–0.016(2)	–0.005(3)	–0.011(2)
C(10)	2*i*	1.1834(7)	0.3876(5)	0.6259(3)	0.032(3)	0.036(3)	0.042(3)	–0.013(2)	–0.010(2)	–0.008(2)
C(11)	2*i*	0.9879(7)	0.3295(5)	0.6987(3)	0.035(3)	0.040(3)	0.034(3)	–0.007(3)	–0.008(2)	–0.010(2)
C(12)	2*i*	0.8465(7)	0.2909(5)	0.6998(3)	0.026(3)	0.043(3)	0.037(3)	–0.001(2)	–0.002(2)	–0.007(2)
C(13)	2*i*	0.9397(7)	0.1141(5)	0.6973(3)	0.037(3)	0.041(3)	0.042(3)	–0.011(3)	–0.012(3)	0.010(3)
C(14)	2*i*	0.9988(8)	0.0297(5)	0.6510(3)	0.047(4)	0.034(3)	0.041(3)	–0.016(3)	–0.014(3)	0.011(2)
C(15)	2*i*	1.1765(9)	–0.0194(4)	0.5574(4)	0.059(4)	0.020(3)	0.054(4)	0.007(3)	–0.020(3)	–0.007(3)
C(16)	2*i*	1.2913(8)	0.0156(5)	0.5033(4)	0.042(4)	0.032(3)	0.050(4)	0.011(3)	–0.015(3)	–0.009(3)
C(17)	2*i*	1.3258(7)	0.1149(5)	0.3997(4)	0.032(3)	0.036(3)	0.053(4)	0.001(3)	–0.001(3)	–0.015(3)
C(18)	2*i*	1.2498(7)	0.1910(5)	0.3492(3)	0.036(3)	0.040(3)	0.037(3)	–0.008(3)	–0.002(2)	–0.010(2)
C(19)	2*i*	–0.034(1)	0.8412(7)	0.0725(7)	0.070(6)	0.050(5)	0.108(8)	0.002(4)	–0.028(6)	–0.003(5)
C(20)	2*i*	0.107(2)	0.8743(9)	0.0330(8)	0.14(1)	0.057(6)	0.12(1)	0.018(8)	0.02(1)	0.027(7)
C(21)	2*i*	0.559(1)	0.0225(7)	0.2169(7)	0.072(6)	0.049(5)	0.114(9)	–0.008(5)	–0.013(6)	–0.018(5)
C(22)	2*i*	0.661(2)	–0.0074(7)	0.2660(5)	0.119(9)	0.050(5)	0.061(5)	–0.032(6)	–0.018(5)	0.002(4)

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References

1. Corbett, J. D.: Polyatomic Zintl Anions of the Post-Transition Elements. Chem. Rev. **85** (1985) 383-397.
2. Fässler, T. F.: The renaissance of homoatomic nine-atom polyhedra of the heavier carbon-group elements Si-Pb. Coord. Chem. Rev. **215** (2001) 347-377.
3. Fässler, T. F.; Schütz, U.: Conformation Isomerism of Nonagermanide Ions. Crystal Structure of Brown and Red [K-([2.2.2]crypt)]$_6$Ge$_9$Ge$_9$ · (ethylenediamine)$_x$ (x = 0.5, 1.5). Inorg. Chem. **38** (1999) 1866-1870.
4. Fässler, T. F.; Hunziker, M.: Ge_9^{3-} and Pb_9^{3-}: Two Novel, Naked, Homopolyatomic Zintl Ions with Paramagnetic Properties. Inorg. Chem. **33** (1994) 5380-5381.
5. Fässler, T. F.; Hunziker, M.; Spahr, M. E.; Lueken, H.; Schilder, H.: Homoatomare Cluster E_9^{3-} mit E = Ge, Sn und Pb: EPR-Spektren, Magnetismus und Elektrochemie. Z. Anorg. Allg. Chem. **626** (2000) 692-700.
6. Belin, C.; Mercier, H.; Angilella, V.: Homoatomic Polyanions of Post Transition-Elements – Synthesis and Structure of Salts Containing the Decagermanide Ge_{10}^{2-} and the Paramagnetic Ge_9^{3-} Anions – Configurational Questions on the Germanium Polyanion Family. New J. Chem. **15** (1991) 931-938.
7. Somer, M.; Carrillo-Cabrera, W.; Peters, E. M.; Peters, K.; von Schnering, H. G.: Tetrarubidium Nonagermanide(4–) Ethylenediamine, $Rb_4[Ge_9]$[en]. Z. Anorg. Allg. Chem. **624** (1998) 1915-1921.
8. Downie, C.; Mao, J.-G.; Guloy, A. M.: Synthesis and Structure of [K^+-(2,2)diaza-[18]-crown-6][K_3Ge_9] · 2Ethylenediamine: Stabilization of the Two-Dimensional Layer $^2_\infty[K_3Ge_9^{1-}]$. Inorg. Chem. **40** (2001) 4721-4725.
9. Hauptmann, R.; Fässler, T. F.: Crystal structure of di[K(18-crown-6)]-dirubidium nonagermanide(4–) diethylenediamine, $[K(C_{12}H_{26}N_2O_4)]_2$-$Rb_2[Ge_9] \cdot 2C_2N_2H_8$. Z. Kristallogr. NCS **218** (2003) 370–372.
10. Xu, L.; Sevov, S. C.: Oxidative Coupling of Deltahedral $[Ge_9]^{4-}$ Zintl Ions. J. Am. Chem. Soc. **121** (1999) 9245-9246.
11. Hauptmann, R.; Fässler, T. F.: Low Dimensional Arrangements of the Zintl Ion $[Ge_9\text{-}Ge_9]^{6-}$ and Chemical Bonding in $[Ge_6]^{2-}$, $[Ge_9\text{-}Ge_9]^{6-}$, and $^1_\infty[Ge_9]^{2-}$. Z. Anorg. Allg. Chem., in press.
12. Ugrinov, A.; Sevov, S. C.: $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$: A Linear Trimer of 27 Germanium Atoms. J. Am. Chem. Soc. **124** (2002) 10990-10991.
13. Downie, C.; Tang, Z.; Guloy, A. M.: An Unprecedented $^1_\infty[Ge_9]^{2-}$ Polymer: A Link between Molecular Zintl Clusters and Solid-State Phases. Angew. Chem. **112** (2000) 346-348; Angew. Chem. Int. Ed. Engl. **29** (2000) 338-340.
14. Nienhaus, A.; Hauptmann, R.; Fässler, T. F.: $^1_\infty[HgGe_9]^{2-}$ – Ein durch Heteroatome kovalent verknüpftes Polymer mit Zintl-Ionen als Bausteinen. Angew. Chem. **114** (2002) 3352-3355; Angew. Chem. Int. Ed. **41** (2002) 3213-3215.
15. Sheldrick, G. M.: SHELXS-97. Program for the solution of crystal structures. University of Göttingen, Germany 1997.
16. Sheldrick, G. M.: SHELXL-97. Program for refining crystal structures. University of Göttingen, Germany 1997.