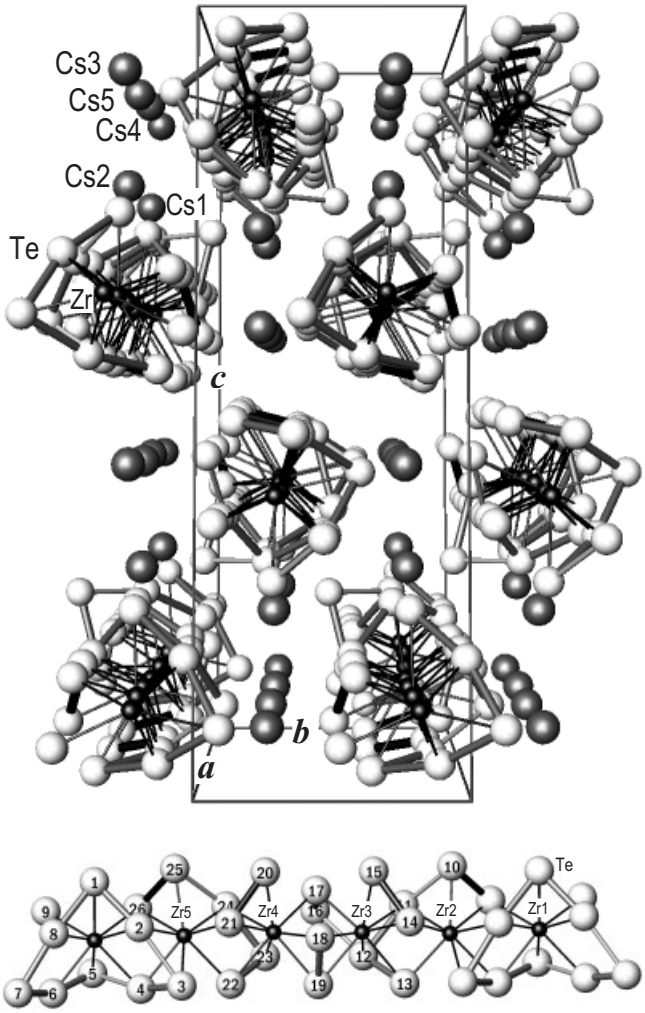
Crystal structure of pentacaesium hexacosatelluridopentazirconate, $Cs_5Zr_5Te_{26}$, *a new polyanionic chalcogenometalate*

N. A. Harringer and K. O. Klepp*

University of Linz, Department of General and Inorganic Chemistry, Altenbergerstraße 69, A-4040 Linz, Austria

Received June 3, 2003, accepted and available on-line July 23, 2003; CSD-No. 409709



Abstract

$Cs_5Te_{26}Zr_5$, monoclinic, $P12_1/c1$ (No. 14), a = 19.39(2) Å, b = 9.548(2) Å, c = 28.06(5) Å, β = 98.51(5)°, V = 5137.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F)$ = 0.047, T = 294 K.

Source of material

The title compound was isolated in the form of lustrous needle shaped crystals from a heterogeneous sample with nominal composition $Cs_3CuZrTe_{14}$ which had been obtained by reacting 416 mg Cs_2Te with appropriate amounts of the corresponding elemental components at 1073 K.

Discussion

$Cs_5Zr_5Te_{26}$ is characterized by a pseudo one-dimensional structure where infinite $[Zr_5Te_{26}]^{5-}$ chains – running along [100] – are arranged in the sense of a distorted hexagonal rod packing (top figure). The translation period of the chain comprises five independent Zr atoms. It is divided into two similar halves by two pseudo mirror planes passing through Te1, Te5, Zr1 and Te16-Te19, respectively. The infinite $[Zr_5Te_{26}]^{5-}$ chain is shown in the bottom figure, where the Te—Te bond lengths are distinguished by different shadings (black: 2.75 Å – 2.80 Å, grey: 2.845 Å – 3.05 Å, light grey: 3.05 Å – 3.22 Å, respectively). Zr—Zr distances within the chain range from 3.839(4) Å to 3.906(4) Å virtually ruling out bonding interactions between the transition metal atoms. All zirconium atoms are in distorted quadratic antiprismatic chalcogen coordinations. The coordination polyhedra are connected via triangular faces, yielding the composition Zr_5Te_{25} (= $(ZrTe_2ZrTe_{6/2})_5$). One Te atom (Te16) is not directly bonded to Zr. Individual Zr—Te bond lengths are in the range of 2.913(3) Å to 3.040(4) Å, with the average value 2.968 Å. As a contrast – due to extensive partial homonuclear bonding – the spread of the Te—Te bonds is surprisingly large. There are only 4 ditelluride pairs with bond lengths indicating single bonds (d(Te9—Te10) = 2.801(4) Å, d(Te14—Te15) = 2.752(2) Å, d(Te20—Te21) = 2.764(2) Å, d(Te25—Te26) = 2.795(3) Å) while 12 Te—Te bonds cluster around values between 2.845(2) Å and 3.021(2) Å which – like in the isostructural hafnium compound $Cs_5Hf_5Te_{26}$ [1] – virtually rules out a rational assignment of the oxidation states through an assessment of Te—Te bonding. The shortest interanionic Te—Te distance is found at a distinctly higher value of d(Te16—Te19) = 3.246 Å indicating only weak bonding interactions between the chains. The 5 independent Cs atoms which separate the chains are in highly irregular chalcogen coordinations by 11 (Cs1, Cs2, Cs5) or 12 (Cs3, Cs4) tellurium atoms, respectively.

Table 1. Data collection and handling.

Crystal:	metallic needle, size 0.05 × 0.10 × 0.35 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	189.60 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	52.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11436, 11104
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 6842
$N(param)_{refined}$:	325
Programs:	SIR92 [2], Crystal Structure [3], ATOMS [4]

* Correspondence author (e-mail: kurt.klepp@jku.at)

Table 2. 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*	0.70810(7)	0.2189(1)	0.27845(5)	0.0361(7)	0.0285(6)	0.0400(7)	–0.0005(5)	0.0114(6)	–0.0059(5)
Cs(2)	4*e*	0.69430(8)	0.7167(2)	0.22314(6)	0.0457(8)	0.0397(8)	0.055(1)	0.0016(6)	0.0093(7)	0.0069(7)
Cs(3)	4*e*	0.45996(8)	0.7360(1)	0.08632(6)	0.0418(8)	0.0267(6)	0.067(1)	–0.0039(6)	0.0250(7)	–0.0041(6)
Cs(4)	4*e*	1.08918(7)	0.7387(1)	0.08387(5)	0.0324(6)	0.0213(6)	0.0499(8)	0.0006(5)	0.0117(6)	–0.0041(5)
Cs(5)	4*e*	0.83235(7)	0.7341(1)	0.08833(5)	0.0410(7)	0.0230(6)	0.0534(8)	0.0013(5)	0.0219(6)	0.0001(6)
Zr(1)	4*e*	0.47416(8)	0.2057(2)	0.12540(6)	0.0123(7)	0.0137(7)	0.0222(8)	–0.0009(6)	0.0042(6)	–0.0010(6)
Zr(2)	4*e*	0.67511(8)	0.1949(2)	0.12499(6)	0.0124(7)	0.0115(7)	0.0244(9)	0.0003(6)	0.0043(6)	0.0009(6)
Zr(3)	4*e*	0.87158(8)	1.2028(2)	0.11874(6)	0.0111(7)	0.0124(7)	0.0218(8)	0.0008(5)	0.0042(6)	–0.0002(6)
Zr(4)	4*e*	0.93015(8)	0.7101(2)	0.38353(6)	0.0123(7)	0.0137(7)	0.0209(8)	0.0002(6)	0.0057(6)	0.0015(6)
Zr(5)	4*e*	0.27230(8)	0.2121(2)	0.12152(6)	0.0128(7)	0.0122(7)	0.0272(9)	0.0008(6)	0.0065(6)	0.0010(6)
Te(1)	4*e*	0.45506(6)	0.3558(1)	0.03271(4)	0.0214(6)	0.0190(6)	0.0265(6)	–0.0009(4)	0.0069(5)	0.0043(5)
Te(2)	4*e*	0.36184(6)	0.1348(1)	0.04704(4)	0.0136(5)	0.0231(6)	0.0258(6)	–0.0003(4)	0.0043(4)	–0.0049(5)
Te(3)	4*e*	0.28024(6)	–0.0911(1)	0.09836(5)	0.0214(6)	0.0132(5)	0.0366(7)	–0.0038(4)	0.0046(5)	–0.0010(5)
Te(4)	4*e*	0.38281(6)	0.0287(1)	0.17515(4)	0.0158(5)	0.0219(6)	0.0340(7)	0.0028(4)	0.0095(5)	0.0087(5)
Te(5)	4*e*	0.49731(6)	0.2160(1)	0.23265(4)	0.0216(6)	0.0315(6)	0.0214(6)	0.0011(5)	0.0045(5)	–0.0043(5)
Te(6)	4*e*	0.58136(6)	0.0225(1)	0.17836(4)	0.0157(5)	0.0220(6)	0.0328(7)	0.0003(4)	0.0052(5)	0.0082(5)
Te(7)	4*e*	0.64846(6)	–0.1052(1)	0.09971(5)	0.0233(6)	0.0122(5)	0.0402(7)	0.0016(4)	0.0131(5)	–0.0032(5)
Te(8)	4*e*	0.55456(6)	0.1182(1)	0.05049(4)	0.0150(5)	0.0227(6)	0.0239(6)	–0.0026(4)	0.0064(4)	–0.0051(5)
Te(9)	4*e*	0.58442(6)	0.4171(1)	0.15629(5)	0.0150(5)	0.0177(6)	0.0396(7)	0.0000(4)	0.0053(5)	–0.0092(5)
Te(10)	4*e*	0.65651(6)	0.4708(1)	0.07879(5)	0.0253(6)	0.0143(5)	0.0367(7)	–0.0016(4)	0.0002(5)	0.0065(5)
Te(11)	4*e*	0.78040(5)	0.4111(1)	0.15975(4)	0.0147(5)	0.0114(5)	0.0295(6)	–0.0001(4)	0.0064(4)	–0.0023(4)
Te(12)	4*e*	0.88585(6)	0.2590(1)	0.22425(4)	0.0192(5)	0.0244(6)	0.0211(6)	0.0040(4)	0.0040(4)	–0.0021(5)
Te(13)	4*e*	0.79074(6)	0.0349(1)	0.18142(4)	0.0163(5)	0.0130(5)	0.0279(6)	0.0003(4)	0.0058(4)	0.0046(4)
Te(16)	4*e*	0.98943(8)	0.5113(2)	0.22793(7)	0.0353(8)	0.0364(8)	0.090(1)	–0.0072(6)	0.0179(8)	–0.0374(9)
Te(14)	4*e*	0.75308(6)	0.1276(1)	0.04560(4)	0.0166(5)	0.0195(5)	0.0239(6)	–0.0022(4)	0.0059(4)	–0.0048(4)
Te(15)	4*e*	0.82570(6)	0.3629(1)	0.02571(4)	0.0255(6)	0.0238(6)	0.0272(6)	–0.0036(5)	0.0061(5)	0.0019(5)
Te(17)	4*e*	0.97065(5)	0.4371(1)	0.12381(4)	0.0158(5)	0.0113(5)	0.0291(6)	0.0003(4)	0.0074(4)	–0.0011(4)
Te(18)	4*e*	1.04224(6)	0.5689(1)	0.44603(5)	0.0169(6)	0.0373(7)	0.0321(7)	0.0036(5)	0.0075(5)	0.0139(6)
Te(19)	4*e*	1.01896(6)	0.4958(1)	0.34472(4)	0.0164(5)	0.0164(5)	0.0277(6)	–0.0008(4)	0.0071(4)	–0.0014(4)
Te(20)	4*e*	1.06924(6)	0.3668(1)	0.02207(4)	0.0241(6)	0.0222(6)	0.0302(6)	0.0038(5)	0.0060(5)	0.0021(5)
Te(21)	4*e*	0.84173(5)	0.6418(1)	0.45692(4)	0.0144(5)	0.0200(6)	0.0243(6)	0.0005(4)	0.0057(4)	0.0042(4)
Te(22)	4*e*	0.81929(6)	0.5476(1)	0.32238(4)	0.0154(5)	0.0166(5)	0.0311(6)	–0.0020(4)	0.0069(5)	–0.0055(5)
Te(23)	4*e*	0.89407(6)	0.7630(1)	0.27890(4)	0.0210(6)	0.0257(6)	0.0233(6)	0.0030(5)	0.0074(5)	0.0026(5)
Te(24)	4*e*	0.82079(5)	0.9225(1)	0.34334(4)	0.0156(5)	0.0125(5)	0.0324(6)	0.0010(4)	0.0050(5)	0.0039(5)
Te(25)	4*e*	0.27940(6)	0.4924(1)	0.07809(5)	0.0218(6)	0.0160(5)	0.0339(7)	0.0024(4)	0.0050(5)	0.0049(5)
Te(26)	4*e*	0.37852(5)	0.4220(1)	0.15724(4)	0.0144(5)	0.0157(5)	0.0315(6)	–0.0004(4)	0.0058(5)	–0.0046(5)

References

1. Pell, M. A.; Ibers, J. A.: New Ternary Group IV Tellurides with Extensive Te-Te Bonding: The Low-Dimensional Compounds $Cs_3Ti_3Te_{11}$ and $Cs_5Hf_5Te_{26}$. Chem. Mater. **8** (1996) 1386-1390.
2. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.: Completion and refinement of crystal structures with SIR92. J. Appl. Crystallogr. **26** (1993) 343-350.
3. Crystal Structure V 2.0, Single Crystal Structure Analysis Software. Molecular Structure Corporation. The Woodlands, TX 77381, USA 2000.
4. Dowty, E.: Atoms 5.0, A Complete Program for Displaying Atomic Structures. By Shape Software, Kingsport, TN 37663, USA 1999.