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sides of the Zr atom; the coordination polyhedron may be described as a distorted quadratic antiprism. The distances between the Si atoms [2.614 (1) Å] are longer than that of a Si—Si single bond (2.35 Å), but comparable with the Si—Si separations in transition-metal disilicides. The Te—Te separations within the Te_4 plane give no indication of significant interactions. The distances between Zr and Te atoms of neighbouring layers [3.957 (1) Å] are too long for Zr—Te bonds. Hence, contrary to the isotypic compounds ZrSiX ($X = \text{S}, \text{Se}$) and ZrGeX ($X = \text{S}, \text{Se}, \text{Te}$), ZrSiTe is best described as a layer compound.

Comment

During a systematic study of the Zr—S, Zr—Se and Zr—Te systems, binary compounds with the composition Zr_4X_3 were obtained (Hahn, Harder, Mutschke & Ness, 1957; Hahn & Ness, 1959). These compounds were later identified as silicide chalcogenides of Zr with the composition ZrSiX ($X = \text{S}, \text{Se}, \text{Te}$) (Jellinek & Hahn, 1962). The first crystal structure determination of tetragonal ZrSiTe used X-ray powder data (Klein-Haneveld & Jellinek, 1964). It was demonstrated that compounds with the formal compositions ZrGeX , HfSiX and HfGeX ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$) are isotypic with ZrSiX and crystallize in the PbFCl -type structure (Onken, Vierheilig & Hahn, 1964). The single-crystal data presented here are in good agreement with the results of Jellinek & Hahn (1962). The Zr—Te interatomic separation is of the order observed in zirconium tellurides

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Structure of the Layer Compound ZrSiTe

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Abstract

Zirconium silicon telluride, ZrSiTe , crystallizes in a layer-type structure which is related to the PbFCl type. The Zr atom is coordinated by four Si and four Te atoms. The Si and Te atoms are arranged in square planes. These planes are situated at opposite

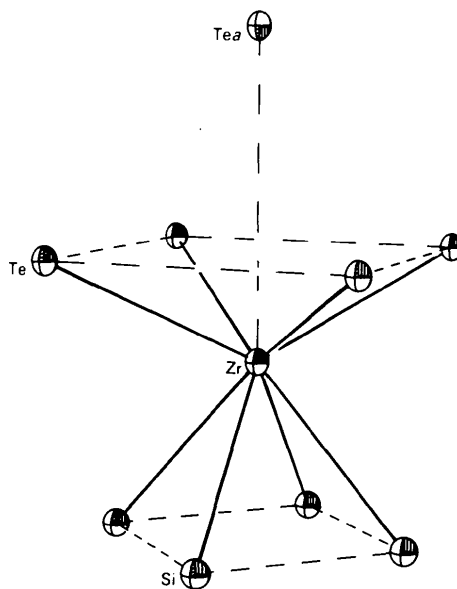


Fig. 1. The coordination polyhedron about the Zr atom. The atom Te_a is in the neighbouring layer. Probability ellipsoids are drawn at the 70% level.

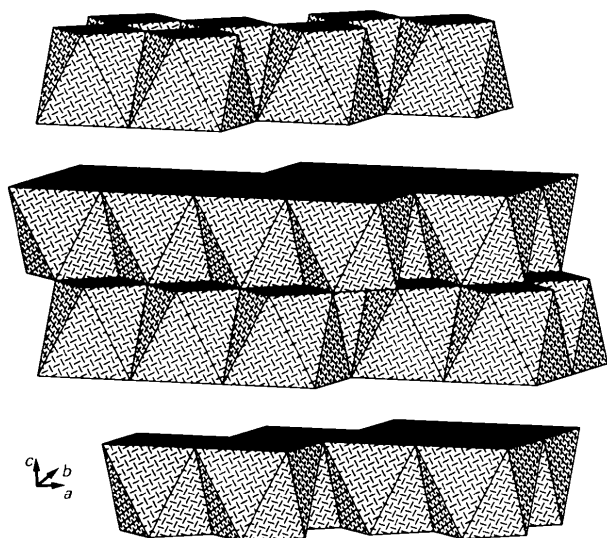


Fig. 2. Polyhedral representation of the structure of ZrSiTe.

(Furuseth, Brattas & Kjekshus, 1975; Keane & Ibers, 1991), whereas the Zr—Si distance is longer than that found in binary zirconium silicides (Schachner, Nowotny & Kudielka, 1954). The Zr—Zr separation of 3.697 (1) Å is about 15% larger than in Zr metal. In the ternary compounds ZrSiX (X = S, Se) and ZrGeX (X = S, Se, Te) the separations between Zr and X atoms in neighbouring layers are comparable with the Zr—X distances within the quadratic antiprism. Hence, the Zr atoms are ninefold coordinated by four Si (Ge) and five X atoms. These compounds show three-dimensional character (Klein-Haneveld & Jellinek, 1964).

The title compound was obtained during the synthesis of ternary zirconium tellurides at elevated temperatures in quartz ampoules. The products always contained appreciable amounts of ZrSiTe. This observation is in agreement with the results of Hahn & Ness (1959). A view of the coordination about the Zr atom is given in Fig. 1. Fig. 2 shows a polyhedral representation of the structure.

Experimental

Crystal data

ZrSiTe
 $M_r = 246.906$
 Tetragonal
 $P4/nmm$
 $a = 3.6974$ (9) Å
 $c = 9.508$ (2) Å
 $V = 129.98$ (6) Å³
 $Z = 2$
 $D_x = 6.309$ Mg m⁻³

Mo K α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 22 reflections
 $\theta = 10.75$ – 13.15°
 $\mu = 15.279$ mm⁻¹
 $T = 295$ K
 Rectangular platelet
 $0.086 \times 0.07 \times 0.016$ mm
 Black

Data collection

Stoe AED 2 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 by integration from crystal shape
 $T_{\min} = 0.175$, $T_{\max} = 0.565$
 1071 measured reflections
 177 independent reflections

175 observed reflections
 $R_{\text{int}} = 0.0273$
 $\theta_{\max} = 32.5^\circ$
 $h = -5 \rightarrow 5$
 $k = 0 \rightarrow 5$
 $l = -14 \rightarrow 14$
 4 standard reflections
 frequency: 180 min
 intensity variation: $\leq 1.4\%$

Refinement

Refinement on F
 $R = 0.017$
 $wR = 0.0147$
 $S = 1.30$
 175 reflections
 10 parameters
 $w = 1/[\sigma^2(F) + 0.00008F^2]$
 $(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 1.45$ e Å⁻³
 $\Delta\rho_{\min} = -2.81$ e Å⁻³

Extinction correction:

$$F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$$

Extinction coefficient:

$$\chi = 0.0063$$
 (4)

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* \cdot a_j^*$$

	x	y	z	U_{eq}
Zr	1/4	1/4	0.7238 (1)	0.0061 (1)
Te	1/4	1/4	0.1399 (1)	0.0059 (1)
Si	3/4	1/4	1/2	0.0074 (2)

Table 2. Selected geometric parameters (Å)

Zr—Te	2.918 (1)	Zr—Tea	3.957 (1)
Zr—Si	2.819 (1)	Zr—Zr	3.697 (1)
Si—Si	2.614 (1)		

Two reflections were omitted from the data set because they were strongly affected by extinction effects. During the refinement no further reflections were suppressed. Computations were performed using *SHELXTL-Plus* (Sheldrick, 1987).

Lists of structure factors, anisotropic displacement parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71546 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1027]

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A Novel Triply Chromium(III)-Substituted Keggin Anion, $[A-\alpha-SiO_4W_9Cr_3(OH_2)_3O_{33}]^{7-}$

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Abstract

The structure determination of $K_3H_4[A-\alpha-SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot 11H_2O$, tripotassium tetrahydrogen triaquatrachromononatungstosilicate undecahydrate, represents the first X-ray analysis of a triply substituted Keggin anion containing low-valent hetero-elements. The CrO_6 and WO_6 polyhedra are discussed on the basis of interatomic distances; for CrO_6 coordination an almost ideal octahedron is observed.

Comment

Recently, Liu *et al.* (1992) reported the synthesis and characterization of trimetallo derivatives of lacunary nonatungstosilicate heteropolyanions. In these anions, $[SiO_4W_9M_3(OH_2)_3O_{33}]^{n-}$, with the well known Keggin structure, main-group or low-valent 3d elements occupy a quarter of all the tungsten positions. Based on the structure of the precursor anion and ^{183}W NMR spectra ($M = Al, Ga$), it is expected, without any crystallographic evidence, that the MO_6 octahedra are corner-shared.

For the similar anion $[B-\alpha-PO_4W_9Ni_3(OH_2)_3O_{33}-WO_2(OH_2)]^{7-}$, the structure has been determined by Gómez-García, Coronado & Ouahab (1992). However, in this case the triply substituted Keggin anion is additionally capped on the NiO_6 octahedra by a $WO_2(OH_2)$ group.

We shall now present the X-ray analysis of $K_3H_4[A-\alpha-SiO_4W_9Cr_3(OH_2)_3O_{33}]\cdot 11H_2O$, which was synthesized by fixing three Cr^{3+} ions on vacant tungsten positions in $[A-\alpha-SiO_4W_9O_{30}]^{10-}$, which effectively constitutes the first ever structure of this type of triply substituted Keggin anion.

The compound was prepared following the procedure of Peng, Qu & Chen (1991), modified by us. After a few days, the repeatedly recrystallized potassium salt (water with some acetone, pH 5) yielded non-disordered crystals, stable in air and suitable for X-ray structural analysis. In the asymmetric unit, one Cr atom is placed in a general position with another in the mirror plane. The centrosymmetric unit of two anions with corner-shared CrO_6 octahedra is given in Fig. 1. The X-ray analysis characterizes the structure of the precursor anion $[A-\alpha-SiO_4W_9O_{30}]^{10-}$ in an indirect way. Until now, only the structure of the isomeric $[A-\beta-SiO_4W_9O_{30}]^{10-}$ anion has been determined (Robert & Tézé, 1981).

The close-bowl packing of the Keggin anion with 40 O atoms is not substantially affected by the tri-substitution. Most of the changes in the structure are related to the metal–oxygen and metal–metal bond distances. As evidenced from the data, the Cr atoms are located in an almost ideal octahedral O-atom environment, in contrast to all observed W-atom positions in polyoxometallate chemistry. The different formal oxidation states of Cr^{3+} and

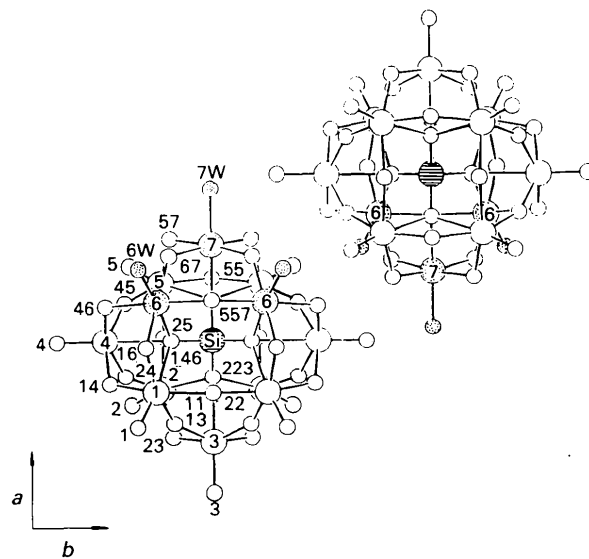


Fig. 1. ORTEP (Johnson, 1965) drawing of $[A-\alpha-SiO_4W_9Cr_3(OH_2)_3O_{33}]^{7-}$ showing the arrangement of the anions in centrosymmetric pairs. Large open circles represent W atoms, small open circles represent O atoms, and the large hatched circle represents Si. Aqua ligands attached to Cr atoms (large shaded circles) are indicated by small shaded circles.