

$\text{Cs}_3\text{Hf}_2(\text{P}_2\text{S}_7)_2(\text{PS}_4)$ 

Andreas Gutzmann, Christian Nätzer and Wolfgang Bensch\*

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

Correspondence e-mail: wbensch@ac.uni-kiel.de

## Key indicators

Single-crystal X-ray study

$T = 180\text{ K}$

Mean  $\sigma(\text{S-P}) = 0.007\text{ \AA}$

$R$  factor = 0.041

$wR$  factor = 0.104

Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The first quaternary hafnium thiophosphate, tricaesium dihafnium pentaphosphorus octadecasulfide,  $\text{Cs}_3\text{Hf}_2\text{P}_5\text{S}_{18}$  was synthesized by reacting  $\text{HfS}_2$  with an *in situ* formed melt of  $\text{Cs}_2\text{S}_3$ ,  $\text{P}_2\text{S}_5$  and S. The crystal structure is composed of a two-dimensional anionic  $[\text{Hf}_2\text{P}_5\text{S}_{18}]^{3-}$  layer and intervening  $\text{Cs}^+$  cations. Each of the two independent  $\text{Hf}^{4+}$  ions is surrounded by seven S atoms forming a distorted pentagonal bipyramid. The  $\text{HfS}_7$  polyhedra are connected by an unusual edge- and corner-sharing arrangement of  $[\text{P}_2\text{S}_7]$  groups and edge-sharing  $[\text{PS}_4]$  tetrahedra into the final double-layered anion.

## Comment

Until now, only a few quaternary alkali metal thiophosphates of group 4 metals have been structurally characterized (Cieren *et al.*, 1994; Do *et al.*, 1996; Derstroff *et al.*, 2002). All quaternary compounds contain titanium as the transition metal. In our investigations of the  $A\text{-}M\text{-}P\text{-}S$  family ( $A$  = alkali metal and  $M$  = group 4 metal), we prepared very recently the first quaternary zirconium thiophosphates, *viz.*  $A_3\text{Zr}_2\text{P}_5\text{S}_{18}$  ( $A$  = Rb, Cs) (Gutzmann *et al.*, 2004), enhancing the range of structures of the  $A\text{-}M\text{-}P\text{-}S$  family. One interesting observation made in the past was that the ternary thiophosphates  $M\text{P}_2\text{S}_6$  with  $M = \text{Ti}, \text{Zr}$  and  $\text{Hf}$  are not isostructural (Jandali *et al.*, 1980; Simon *et al.*, 1982, 1985; Lott *et al.*, 1999). This observation was also made in the quaternary thiophosphates with the general formula  $A_3M_2P_5S_{18}$ , where the Ti compound is structurally quite different from the Zr compound. In our effort to investigate and determine the relationships between the cation size, the  $M:S$  ratio and the dimensionality of the structures in group 4 metal thiophosphates, we have obtained the new compound  $\text{Cs}_3\text{Hf}_2\text{P}_5\text{S}_{18}$ , which is isostructural with the Zr compound.

The crystal structure of  $\text{Cs}_3\text{Hf}_2\text{P}_5\text{S}_{18}$  is built up of  $[\text{Hf}_2\text{P}_5\text{S}_{18}]^{3-}$  layers extending in the (001) plane and charge-

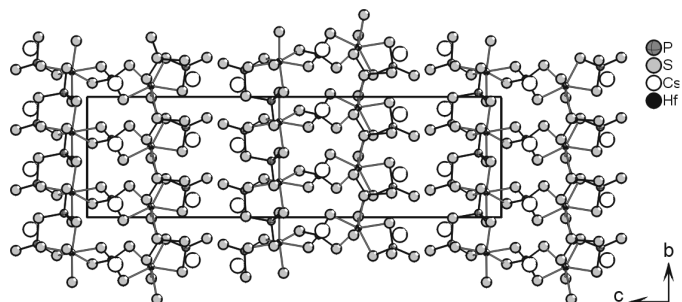


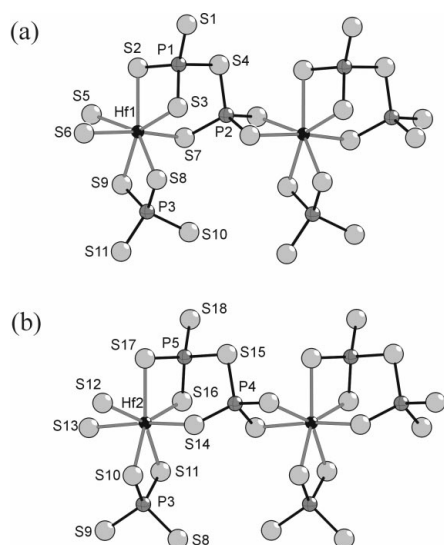
Figure 1

The crystal structure of  $\text{Cs}_3\text{Hf}_2\text{P}_5\text{S}_{18}$ , viewed in the direction of the crystallographic  $a$  axis.

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**Figure 2**  
Interconnection of the two distinct  $\text{HfS}_7$  polyhedra *via* pentadentate  $[\text{P}_2\text{S}_7]$  groups.

compensating  $\text{Cs}^+$  cations. The main feature of this structure type is the presence of  $\text{HfS}_7$  polyhedra which are interconnected *via* pentadentate  $[\text{P}_2\text{S}_7]$  groups and tetradentate  $[\text{PS}_4]$  tetrahedra into a double-layered structure. Each of the two distinct  $\text{Hf}^{4+}$  ions is surrounded by seven S atoms forming a distorted pentagonal bipyramid. The mean Hf–S bond lengths of 2.617 (5) Å in the  $\text{Hf1S}_7$  polyhedron and 2.621 (5) Å for  $\text{Hf2S}_7$  are in good agreement with the sum of the ionic radii [1.84 Å for  $\text{S}^{2-}$  and 0.76 Å for  $\text{Hf}^{4+}$  (CN7); Shannon, 1976]. The  $\text{Hf1S}_7$  and  $\text{Hf2S}_7$  polyhedra are linked *via* one  $[\text{P}_2\text{S}_7]$  group that acts in an unusual pentadentate fashion. Each of the  $\text{HfS}_7$  groups shares two common edges and one corner with two symmetry-related  $[\text{P}_2\text{S}_7]$  units. Furthermore, the  $\text{Hf1S}_7$  and  $\text{Hf2S}_7$  polyhedra are interconnected *via* tetradentate  $[\text{PS}_4]$  tetrahedra into the final double-layered structure. The average P–S distances in the two unique pyrothiophosphate ligands and the  $[\text{PS}_4]$  tetrahedra are 2.050, 2.052 and 2.038 Å. The longest P–S bonds in the  $[\text{P}_2\text{S}_7]$  groups are observed for S atoms having bonds to two P atoms. The S–P–S angles in the thiophosphate ligands exhibit a significant distortion. The three crystallographically independent  $\text{Cs}^+$  cations are surrounded either by nine S atoms (average Cs1–S distance 3.739 Å and average Cs3–S distance 3.735 Å) or by ten S atoms (average Cs2–S distance 3.780 Å); these distances agree well with the sum of the ionic radii. The charge balance of the compound may be formulated as  $[\text{Cs}^+]_3[\text{Hf}^{4+}]_2[\text{PS}_4^{3-}][\text{P}_2\text{S}_7^{4-}]_2$ .

## Experimental

The compound  $\text{Cs}_3\text{Hf}_2\text{P}_5\text{S}_{18}$  was obtained by the reaction of  $\text{Cs}_2\text{S}_3$  (0.3 mmol),  $\text{HfS}_2$  (0.15 mmol),  $\text{P}_2\text{S}_5$  (0.45 mmol) and S (1.5 mmol).  $\text{Cs}_2\text{S}_3$  was prepared from stoichiometric amounts of Cs and S in liquid ammonia under an argon atmosphere. The starting materials were loaded into a quartz tube which was evacuated ( $10^{-3}$  mbar) and flame-sealed. The ampoule was heated to 873 K within 24 h. After 4 d, the sample was cooled down to 523 K at  $2 \text{ K h}^{-1}$  and then to

room temperature within 10 h. To remove unreacted  $\text{Cs}_x\text{P}_y\text{S}_z$ , the resultant melt was washed with dry *N,N*-dimethylformamide and diethyl ether. The product was dried in a vacuum and consisted of light-yellow plate-like crystals which are air- and moisture-sensitive.

## Crystal data

$\text{Cs}_3\text{Hf}_2(\text{P}_2\text{S}_7)_2(\text{PS}_4)$   
 $M_r = 1487.64$   
 Monoclinic, *Cc*  
 $a = 9.3168$  (4) Å  
 $b = 9.8985$  (6) Å  
 $c = 34.0830$  (17) Å  
 $\beta = 94.236$  (6)°  
 $V = 3134.6$  (3) Å<sup>3</sup>  
 $Z = 4$

$D_x = 3.152 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 8000 reflections  
 $\theta = 1.3$ – $23.3^\circ$   
 $\mu = 11.51 \text{ mm}^{-1}$   
 $T = 180$  (2) K  
 Plate, yellow  
 $0.2 \times 0.2 \times 0.1 \text{ mm}$

## Data collection

Stoe IPDS diffractometer  
 $\varphi$  scans  
 Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 1998)  
 $T_{\min} = 0.120$ ,  $T_{\max} = 0.312$   
 9627 measured reflections

4211 independent reflections  
 4119 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$   
 $\theta_{\max} = 23.1^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -10 \rightarrow 10$   
 $l = -37 \rightarrow 37$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.104$   
 $S = 1.15$   
 4211 reflections  
 254 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 298.6042P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

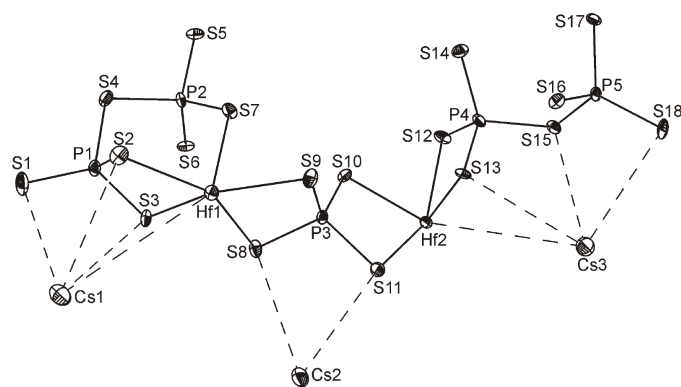
$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.82 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -1.87 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.00031 (3)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.010 (13); 2064 Friedel pairs

**Table 1**

Selected geometric parameters (Å, °).

Hf1–S7	2.554 (5)	P1–S4	2.172 (8)
Hf1–S6 <sup>i</sup>	2.586 (5)	P2–S7	2.023 (7)
Hf1–S9	2.604 (5)	P2–S5	2.039 (7)
Hf1–S8	2.615 (5)	P2–S6	2.046 (7)
Hf1–S3	2.618 (5)	P2–S4	2.115 (7)
Hf1–S2	2.632 (5)	P3–S9	2.017 (7)
Hf1–S5 <sup>i</sup>	2.713 (5)	P3–S10	2.037 (7)
Hf2–S14 <sup>ii</sup>	2.570 (5)	P3–S8	2.047 (7)
Hf2–S13	2.574 (5)	P3–S11	2.051 (7)
Hf2–S11	2.597 (5)	P4–S14	2.028 (8)
Hf2–S16 <sup>ii</sup>	2.611 (5)	P4–S12	2.031 (7)
Hf2–S17 <sup>iii</sup>	2.640 (5)	P4–S13	2.045 (7)
Hf2–S10	2.644 (5)	P4–S15	2.132 (7)
Hf2–S12	2.712 (5)	P5–S18	1.982 (8)
P1–S1	1.969 (8)	P5–S17	2.014 (8)
P1–S2	2.010 (7)	P5–S16	2.024 (7)
P1–S3	2.032 (8)	P5–S15	2.160 (8)
S1–P1–S2	119.8 (3)	S9–P3–S11	113.0 (3)
S1–P1–S3	116.4 (4)	S10–P3–S11	103.0 (3)
S2–P1–S3	101.9 (3)	S8–P3–S11	111.6 (3)
S1–P1–S4	103.4 (3)	S14–P4–S12	107.1 (3)
S2–P1–S4	105.1 (3)	S14–P4–S13	115.0 (3)
S3–P1–S4	109.6 (3)	S12–P4–S13	107.2 (3)
S7–P2–S5	105.7 (3)	S14–P4–S15	112.9 (3)
S7–P2–S6	115.8 (3)	S12–P4–S15	107.1 (3)
S5–P2–S6	108.2 (3)	S13–P4–S15	107.1 (3)
S7–P2–S4	113.3 (3)	S18–P5–S17	119.1 (3)
S5–P2–S4	106.2 (3)	S18–P5–S16	115.1 (3)
S6–P2–S4	107.1 (3)	S17–P5–S16	101.8 (3)
S9–P3–S10	114.0 (3)	S18–P5–S15	103.6 (3)
S9–P3–S8	103.6 (3)	S17–P5–S15	106.6 (3)
S10–P3–S8	111.9 (3)	S16–P5–S15	110.4 (3)

Symmetry codes: (i)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (ii)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ .



**Figure 3**  
Perspective view of the asymmetric unit of the title compound with the atomic labeling. Ellipsoids are drawn at the 50% probability level.

The absolute structure was determined and, according to the Flack  $x$  test, is in agreement with the selected setting. In addition, refinement of the inverse structure leads to significantly poorer reliability factors ( $R$  for all 4119  $F_o > 4\sigma(F_o) = 0.071$ ;  $wR$  for all reflections = 0.169).

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); soft-

ware used to prepare material for publication: *CIFTAB* in *SHELXTL* (Bruker, 1998).

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## References

- Brandenburg, K. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cieren, X., Angenault, J., Couturier, J.-C. & Quarton, M. (1994). *Powder Diffr.* **9**, 105–107.
- Derstroff, V., Tremel, W., Regelsky, G., Schmedt auf der Gönne, J. & Eckert, H. (2002). *Solid State Sci.* **4**, 731–745.
- Do, J., Lee, K. & Yun, H. (1996). *J. Solid State Chem.* **125**, 30–36.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gutzmann, A., Näther, C. & Bensch, W. (2004). *Solid State Sci.* In the press.
- Jandali, M. Z., Eulenberger, G. & Hahn, H. (1980). *Z. Anorg. Allg. Chem.* **470**, 39–44.
- Lott, D. R., Fincher, T., LeBret, G. C., Cleary, D. A. & Breneman, G. L. (1999). *J. Solid State Chem.* **143**, 239–245.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Simon, A., Hahn, H. & Peters, K. (1985). *Z. Naturforsch. Teil B*, **40**, 730–732.
- Simon, A., Peters, K., Peters, E.-M. & Hahn, H. (1982). *Z. Anorg. Allg. Chem.* **491**, 295–300.
- Stoe & Cie (1998). *IPDS Program Package* (Version 2.89), *X-SHAPE* (Version 1.03) and *X-RED32* (Version 1.03). Stoe & Cie, Darmstadt, Germany.