

The two-dimensional thiophosphate CsCrP₂S₇

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 Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(\text{S-P}) = 0.002$ Å; R factor = 0.029; wR factor = 0.073; data-to-parameter ratio = 24.4.

The quaternary title compound, caesium chromium(III) heptathiodiphosphate(V), CsCrP₂S₇, has been synthesized using the reactive halide flux method. It is isotypic with other AMP₂S₇ ($A = \text{alkali metal}$; $M = \text{Cr, V or In}$) structures and consists of two-dimensional $\infty^2[\text{CrP}_2\text{S}_7]^-$ layers extending parallel to (001) which are separated from each other by Cs⁺ ions (symmetry 2). The layer is built up from slightly distorted octahedral [CrS₆] units (symmetry 2) and bent [P₂S₇] units consisting of two corner-sharing [PS₄] tetrahedra. The [CrS₆] octahedra share two edges and two corners with the [PS₄] tetrahedra. There are only van der Waals interactions present between the layers. The Cs⁺ ions are located in this van der Waals gap and stabilize the structure through weak ionic interactions. The classical charge balance of the title compound can be expressed as [Cs⁺][Cr³⁺][P⁵⁺]₂[S²⁻]₇.

Related literature

For AMP₂S₇-related quaternary thiophosphates, see: Kopnin *et al.* (2000) for KMP₂S₇ ($M = \text{Cr, V, In}$); Durand *et al.* (1993) for RbVP₂S₇; Gutzmann *et al.* (2005) for CsVP₂S₇. For the related mixed-metallic phase KV_{1-x}Cr_xP₂S₇, see: Sekizawa *et al.* (2004). Related structures were reported by Coste *et al.* (2001); Derstroff *et al.* (2002); Toffoli *et al.* (1982); Wang *et al.* (1989).

Experimental

Crystal data

CrCsP ₂ S ₇	$V = 548.50$ (8) Å ³
$M_r = 471.34$	$Z = 2$
Monoclinic, $C2$	Mo $K\alpha$ radiation
$a = 8.5867$ (7) Å	$\mu = 5.87$ mm ⁻¹
$b = 9.5461$ (7) Å	$T = 290$ K
$c = 6.7504$ (6) Å	$0.14 \times 0.02 \times 0.02$ mm
$\beta = 97.572$ (3)°	

Data collection

Rigaku R-AXIS RAPID diffractometer	2714 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1268 independent reflections
$T_{\min} = 0.608$, $T_{\max} = 1.000$	1052 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	$\Delta\rho_{\text{max}} = 1.01$ e Å ⁻³
$wR(F^2) = 0.073$	$\Delta\rho_{\text{min}} = -1.09$ e Å ⁻³
$S = 1.18$	Absolute structure: Flack (1983), 593 Friedel pairs
1268 reflections	Flack parameter: -0.01 (3)
52 parameters	
1 restraint	

Table 1

Selected geometric parameters (Å, °).

Cr–S1	2.414 (2)	P–S2	2.024 (3)
Cr–S2	2.440 (2)	P–S3	2.012 (2)
Cr–S3 ⁱ	2.430 (2)	P–S4	2.134 (2)
P–S1	2.025 (3)		
P ⁱⁱ –S4–P	107.50 (14)		

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

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: locally modified version of *ORTEP* (Johnson, 1965); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2382).

References

- Coste, S., Kopnin, E., Evain, M., Jobic, S., Payen, C. & Brec, R. (2001). *J. Solid State Chem.* **162**, 195–203.
- Derstroff, V., Enslin, J., Ksenofontov, V., Güttlich, P. & Tremel, W. (2002). *Z. Anorg. Allg. Chem.* **628**, 1346–1354.
- Durand, E., Evain, M. & Brec, R. (1993). *J. Solid State Chem.* **102**, 146–155.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gutzmann, A., Näther, C. & Bensch, W. (2005). *Acta Cryst.* **E61**, i6–i8.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Kopnin, E., Coste, S., Jobic, S., Evain, M. & Brec, R. (2000). *Mater. Res. Bull.* **35**, 1401–1410.
- Rigaku (2006). *RAPID-AUTO* Manual, Rigaku Corporation, Tokyo, Japan.
- Sekizawa, K., Sashida, M., Takano, Y., Takahashi, Y. & Takase, K. (2004). *J. Magn. Magn. Mater.* **272–276**, e597–e598.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Toffoli, P., Khodadad, P. & Rodier, N. (1982). *Acta Cryst.* **B38**, 2374–2378.
- Wang, Y. P., Lii, K. H. & Wang, S. L. (1989). *Acta Cryst.* **C45**, 1417–1418.

supporting information

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The two-dimensional thiophosphate CsCrP₂S₇

Kyounghee Kim, Jooran Na and Hoseop Yun

S1. Comment

During an attempt to prepare new chromium thiophosphates with the use of halide fluxes, a new compound was isolated. Here we report the synthesis and structure of the new layered quaternary thiophosphate, CsCrP₂S₇.

The title compound is a new member of the previously reported isotypic AMP₂S₇ family (*A* = alkali metal; *M* = Cr, V, or In) (Kopnin *et al.*, 2000; Durand *et al.*, 1993; Gutzmann *et al.*, 2005, Sekizawa *et al.*, 2004). The structure of CsCrP₂S₇ consists of layers with composition $\infty^2[\text{CrP}_2\text{S}_7]^-$ which are composed of [CrS₆] octahedra and bent [P₂S₇⁴⁻] units made up of two corner-sharing [PS₄] tetrahedra. As usually found in other chromium sulfides (Derstroff *et al.*, 2002), each Cr atom is surrounded by six S atoms in a (slightly distorted) octahedral arrangement. In the title compound they share two edges and two corners with the [PS₄] tetrahedra to form the two-dimensional infinite layer extending parallel to (001) (Fig. 1). There are only van der Waals interactions between the layers and the Cs⁺ ions in this van der Waals gap stabilize the structure through weak ionic interactions (Fig. 2).

While both the [CrS₆] octahedron and the [PS₄] tetrahedron show angular distortions, the Cr—S and P—S distances are rather regular and in good agreement with those found in other related phases (e.g. Coste *et al.*, 2001). Atom S4 is bridging two P atoms in the [P₂S₇⁴⁻] units. The bridging P—S4 bond is longer than those of the terminal bonds, a characteristic feature for two condensed PS₄ tetrahedra (Toffoli *et al.*, 1982) or PO₄ tetrahedra (Wang *et al.*, 1989).

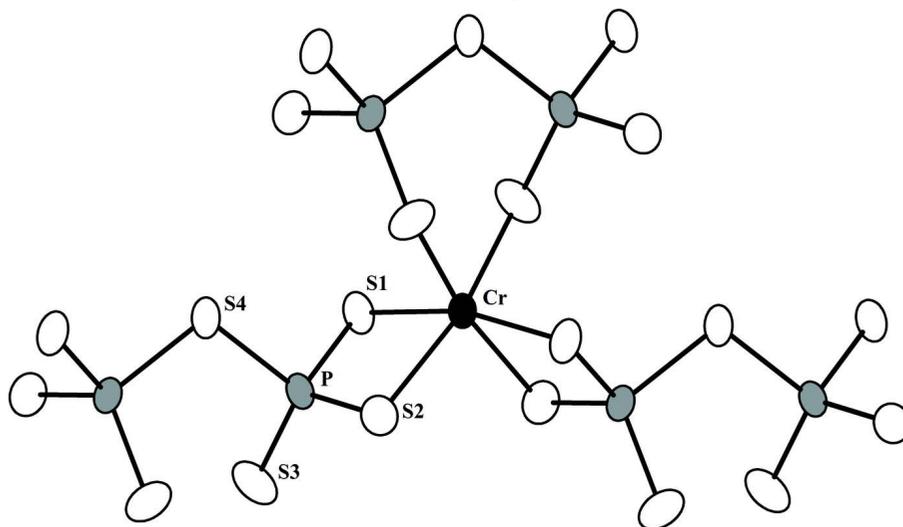
The Cs⁺ ion is surrounded by twelve S atoms if an arbitrarily chosen cut-off of 4.2 Å for the Cs—S bonding interactions is used. The anharmonic behavior of the alkali metal ion, as observed in the isotypic K or Rb analogues (Kopnin *et al.*, 2000; Durand *et al.*, 1993), is not found here. The harmonic behavior of the Cs⁺ ion in the title compound could be due to the larger ionic radius and hence to a larger coordination number (Gutzmann *et al.*, 2005). The classical charge balance of the title compound can be expressed as [Cs⁺][Cr³⁺][P⁵⁺]₂[S²⁻]₇.

S2. Experimental

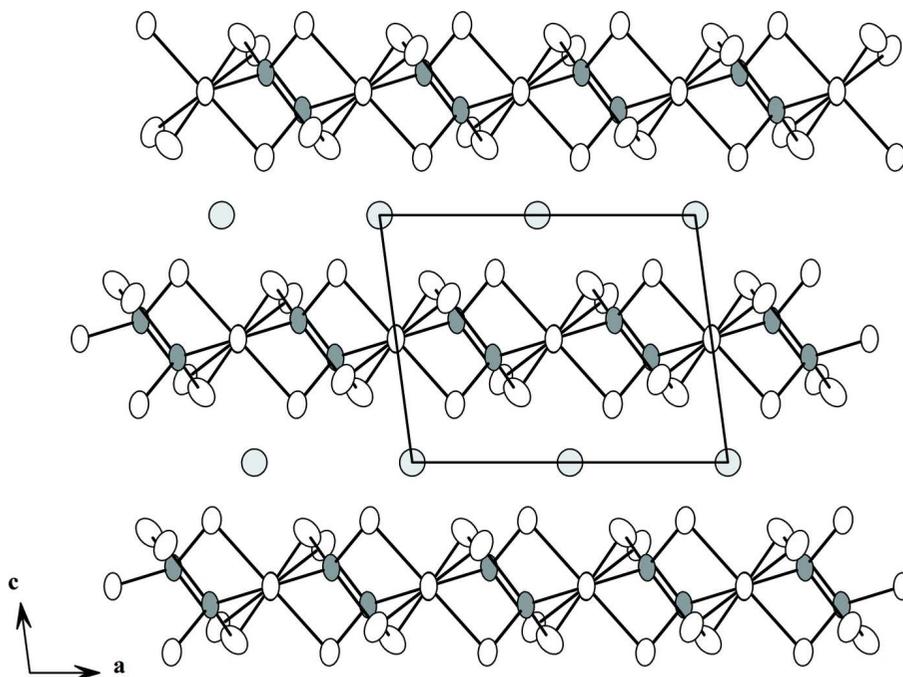
The title compound, CsCrP₂S₇, was prepared by the reaction of the elemental Cr, P and S with the use of the reactive alkali metal halide flux technique. A combination of the pure elements, Cr powder (CERAC 99.95%), P powder (CERAC 99.5%) and S powder (Aldrich 99.999%) were mixed in a fused silica tube in a molar ratio of Cr: P: S = 1: 2: 6 with CsCl/LiCl. The mass ratio of the reactants and the alkali halide flux was 1: 3. The tube was evacuated to 0.133 Pa, sealed and heated gradually (50 K/h) to 923 K, where it was kept for 72 h. The tube was cooled to 473 K at 3 K/h and then was quenched to room temperature. The excess halides were removed with distilled water and dark brown needle shaped crystals were obtained. The crystals are stable in air and water. Semi-qualitative analysis of the crystals with XRF indicated the presence of Cs, Cr, P, and S. No other element was detected.

S3. Refinement

A difference Fourier synthesis calculated with phase based on the final parameters shows that the highest residual electron density ($1.01 \text{ e}/\text{\AA}^3$) is 0.89 \AA from the Cs site and the deepest hole ($-1.09 \text{ e}/\text{\AA}^3$) is 1.74 \AA from the S3 site.

**Figure 1**

The interconnection mode of the $[\text{CrS}_6]$ octahedron and the $[\text{P}_2\text{S}_7]^{4-}$ units with the atom labelling scheme. Displacement ellipsoids are drawn at the 80% probability level.

**Figure 2**

A perspective view of CsCrP_2S_7 down the b axis showing the stacking of the layers. Filled, dark gray, pale gray, and open circles represent Cr, P, Cs, and S atoms, respectively. The Cs—S bonds are omitted for clarity. The displacement ellipsoids are drawn at the 80% probability level.

caesium chromium(III) heptathiodiphosphate(V)

Crystal data

CrCsP₂S₇

$M_r = 471.34$

Monoclinic, *C*2

Hall symbol: C 2y

$a = 8.5867$ (7) Å

$b = 9.5461$ (7) Å

$c = 6.7504$ (6) Å

$\beta = 97.572$ (3)°

$V = 548.50$ (8) Å³

$Z = 2$

$F(000) = 442$

$D_x = 2.854$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10764 reflections

$\theta = 3.0$ – 27.5°

$\mu = 5.87$ mm⁻¹

$T = 290$ K

Needle, dark brown

$0.14 \times 0.02 \times 0.02$ mm

Data collection

Rigaku R-AXIS RAPID

diffractometer

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.608$, $T_{\max} = 1.000$

2714 measured reflections

1268 independent reflections

1052 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -10 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.073$

$S = 1.18$

1268 reflections

52 parameters

1 restraint

$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.2322P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.01$ e Å⁻³

$\Delta\rho_{\min} = -1.09$ e Å⁻³

Absolute structure: Flack (1983), 593 Friedel

pairs

Absolute structure parameter: -0.01 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs	0.5	0.39716 (9)	0	0.0432 (2)
Cr	0	0.48837 (14)	0.5	0.0198 (4)
P	0.3006 (2)	0.63947 (16)	0.4247 (3)	0.0188 (4)
S1	0.15938 (19)	0.51649 (17)	0.2337 (3)	0.0235 (4)
S2	0.1839 (2)	0.65997 (17)	0.6648 (3)	0.0272 (5)
S3	0.3619 (2)	0.81248 (18)	0.2834 (3)	0.0283 (5)
S4	0.5	0.5073 (3)	0.5	0.0218 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs	0.0254 (4)	0.0753 (6)	0.0289 (4)	0	0.0042 (3)	0
Cr	0.0113 (8)	0.0170 (7)	0.0317 (10)	0	0.0048 (7)	0
P	0.0110 (9)	0.0179 (8)	0.0274 (11)	-0.0028 (6)	0.0022 (8)	-0.0004 (8)
S1	0.0149 (8)	0.0271 (9)	0.0291 (10)	-0.0051 (7)	0.0053 (8)	-0.0056 (8)
S2	0.0235 (11)	0.0249 (9)	0.0355 (12)	-0.0039 (7)	0.0127 (9)	-0.0090 (9)
S3	0.0258 (10)	0.0247 (9)	0.0319 (11)	-0.0102 (8)	-0.0056 (9)	0.0070 (9)
S4	0.0119 (11)	0.0249 (13)	0.0288 (15)	0	0.0039 (10)	0

Geometric parameters (\AA , $^\circ$)

Cr—S1 ⁱ	2.414 (2)	P—S1	2.025 (3)
Cr—S1	2.414 (2)	P—S2	2.024 (3)
Cr—S2	2.440 (2)	P—S3	2.012 (2)
Cr—S2 ⁱ	2.440 (2)	P—S4	2.134 (2)
Cr—S3 ⁱⁱ	2.430 (2)	S3—Cr ^{iv}	2.430 (2)
Cr—S3 ⁱⁱⁱ	2.430 (2)	S4—P ^v	2.134 (2)
S1 ⁱ —Cr—S1	167.23 (10)	S3 ⁱⁱⁱ —Cr—S2 ⁱ	166.77 (6)
S1 ⁱ —Cr—S3 ⁱⁱ	104.20 (7)	S2—Cr—S2 ⁱ	95.64 (10)
S1—Cr—S3 ⁱⁱ	84.74 (7)	S3—P—S2	119.23 (11)
S1 ⁱ —Cr—S3 ⁱⁱⁱ	84.74 (7)	S3—P—S1	110.24 (12)
S1—Cr—S3 ⁱⁱⁱ	104.20 (7)	S2—P—S1	104.37 (10)
S3 ⁱⁱ —Cr—S3 ⁱⁱⁱ	92.60 (9)	S3—P—S4	110.27 (11)
S1 ⁱ —Cr—S2	88.98 (7)	S2—P—S4	109.45 (11)
S1—Cr—S2	82.44 (6)	S1—P—S4	101.73 (10)
S3 ⁱⁱ —Cr—S2	166.77 (6)	P—S1—Cr	86.60 (9)
S3 ⁱⁱⁱ —Cr—S2	87.38 (7)	P—S2—Cr	85.93 (9)
S1 ⁱ —Cr—S2 ⁱ	82.44 (6)	P—S3—Cr ^{iv}	114.79 (11)
S1—Cr—S2 ⁱ	88.98 (7)	P ^v —S4—P	107.50 (14)
S3 ⁱⁱ —Cr—S2 ⁱ	87.38 (7)		

Symmetry codes: (i) $-x, y, -z+1$; (ii) $x-1/2, y-1/2, z$; (iii) $-x+1/2, y-1/2, -z+1$; (iv) $x+1/2, y+1/2, z$; (v) $-x+1, y, -z+1$.