

K₉CeP₄S₁₆, a new thiophosphate of cerium with discrete [Ce(PS₄)₄]⁹⁻ anions

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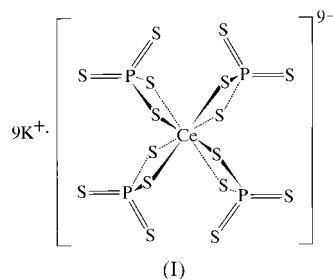
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The structure of nonapotassium cerium tetraphosphorus hexadecasulfide, a zero-dimensional material isostructural with Rb₉CeP₄Se₁₆, is reported.

Comment

In the quest for new Ce-containing materials with interesting chromatic properties, the K/Ce/P/S system has been explored. Hence, the title compound, K₉Ce^{III}P₄S₁₆^{-II}, (I), has been synthesized and structurally characterized. This yellow solid, isostructural with Rb₉CeP₄Se₁₆ (Chondroudis & Kanatzidis, 2000), contains discrete [Ce(PS₄)₄]⁹⁻ anions built upon [CeS₈] triangular dodecahedral polyhedra sharing distinct edges with four [PS₄] tetrahedra. The resulting arrangement of this metal complex exhibits a *D*_{2d} local symmetry. As cerium(III) and potassium(I) have similar ionic radii and since Ce and K5 sites are identical, a small substitution of Ce by K and, complementarily, of K by Ce is observed. All distances and angles are as expected, except for a small shrinking of the K5···S average distance due to the Ce partial substitution.



Experimental

Ce₂S₃ (0.1795 g, 0.5 mmol), P (0.0591 g, 1.9 mmol), K₂S (0.0932 g, 2.4 mmol) and S (0.1682 g, 5.2 mmol) were thoroughly mixed and sealed under vacuum in a silica tube. The reaction mixture was heated to 1073 K at a rate of 4 K h⁻¹, maintained at this temperature for 7 d and then cooled to room temperature at a rate of 4 K h⁻¹. The obtained yellow plate-like crystals are air-sensitive and decompose in presence of water. A single crystal was sealed in a quartz capillary in an argon dry box.

Crystal data

K ₉ CeP ₄ S ₁₆	<i>D</i> _x = 2.389 Mg m ⁻³
<i>M</i> _r = 1128.86	Mo <i>K</i> α radiation
Monoclinic, <i>C</i> 2/ <i>c</i>	Cell parameters from 2000 reflections
<i>a</i> = 20.242 (3) Å	<i>θ</i> = 2–24°
<i>b</i> = 9.788 (1) Å	<i>μ</i> = 3.911 mm ⁻¹
<i>c</i> = 17.524 (2) Å	<i>T</i> = 300 K
<i>β</i> = 115.36 (1)°	Block, yellow
<i>V</i> = 3137.4 (8) Å ³	0.20 × 0.18 × 0.07 mm
<i>Z</i> = 4	

Data collection

Stoe IPDS diffractometer	4324 reflections with <i>F</i> ² > 2σ(<i>F</i> ²)
<i>ω</i> scans	<i>R</i> _{int} = 0.036
Absorption correction: analytical (Becker & Coppens, 1974)	<i>θ</i> _{max} = 27.89°
<i>T</i> _{min} = 0.584, <i>T</i> _{max} = 0.865	<i>h</i> = –26 → 26
22 263 measured reflections	<i>k</i> = –12 → 12
5481 independent reflections	<i>l</i> = –22 → 22

Refinement

Refinement on <i>F</i> ²	139 parameters
<i>R</i> (<i>F</i>) = 0.026	<i>w</i> = 1/(σ ² <i>I</i> + 0.001024 <i>I</i> ²)
<i>wR</i> (<i>F</i> ²) = 0.061	(Δ/σ) _{max} = 0.005
<i>S</i> = 1.12	Δρ _{max} = 1.15 e Å ⁻³
5481 reflections	Δρ _{min} = –0.98 e Å ⁻³

The structure is twinned by merohedry (twofold axis along *c*), twinning domain ratio refined to 0.5175 (6) and 0.4825.

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *JANA98* (Petricek & Dusek, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: *JANA98*; software used to prepare material for publication: *JANA98*.

References

- Altomare, A., Cascarano, C., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Burla, M. C., Polidori, G., Camalli, M. & Spagna, R. (1997). *SIR97*. University of Bari, Italy.
- Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
- Chondroudis, K. & Kanatzidis, M. (2000). Private communication.
- Petricek, V. & Dusek, M. (1998). *JANA98*. Institute of Physics, Prague, Czech Republic.
- Stoe & Cie (1996). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.