

## Pr<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>]: A link between two non-isotypic relatives

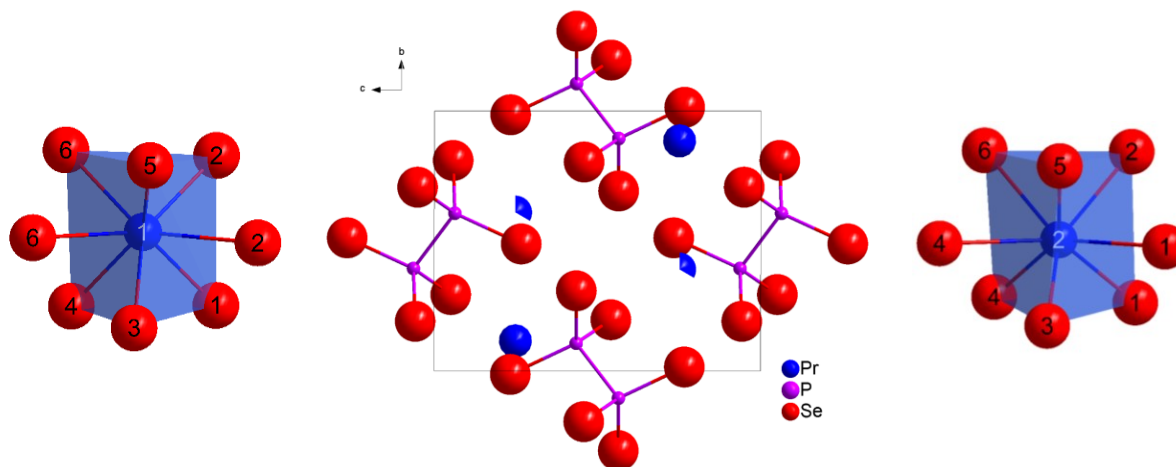
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In 2002, Kanatzidis et al. synthesized and characterized the rare-earth metal(III) hexaselenidodiphosphate(IV) Ce<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>], which crystallizes monoclinically in the space group  $P2_1/c$  [1]. Schleid et al. succeeded to find with Nd<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] [2,3] a further representative, which showed the same structured formula, but adopts a different structure type. It crystallizes in the triclinic space group  $P\bar{1}$  with a modified NaYb[P<sub>2</sub>S<sub>6</sub>]-type structure [3], whilst Ce<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] principally mimics the NaCe[P<sub>2</sub>Se<sub>6</sub>]-type structure [1]. Here we present the gap-filling Pr<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>], which also crystallizes triclinically in the space group  $P\bar{1}$  with  $a = 685.32(5)$  pm,  $b = 759.41(6)$  pm,  $c = 962.56(7)$  pm,  $\alpha = 90.087(3)^\circ$ ,  $\beta = 91.723(3)^\circ$  and  $\gamma = 90.034(3)^\circ$  for  $Z = 2$  at 293 K (CSD number: 2089248), just like Nd<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>]. An extended unit cell of the title compound is depicted in Figure 1 (mid) with highlighted [P<sub>2</sub>Se<sub>6</sub>]<sup>4-</sup>-units, which occur in staggered conformation, very characteristic for hexaselenidodiphosphates(IV). The interatomic distances within these ethane-like anions are also well in the usual range ( $d(\text{P-P}) = 220 - 221$  pm,  $d(\text{P-Se}) = 218 - 220$  pm). The environment of the two distinct Pr<sup>3+</sup> cations resemble bicapped trigonal prisms with distances between praseodymium and selenium from 303 to 337 pm for C.N. = 8 (Figure 1, left and right). Bicapped trigonal prisms are also found in the neighboring compounds Ce<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] and Nd<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] with very similar interatomic Ln–Se distances. Whilst in the neodymium and praseodymium derivatives these [LnS<sub>8</sub>]<sup>13-</sup> polyhedra are edge-connected to form single chains for every individual cation (Ln1 and Ln2), which finally fuse to a framework, a three-dimensional network immediately emerges for the cerium compound from selenium polyhedra of the three crystallographically different Ce<sup>3+</sup> cations with C.N. = 8. All three compounds have cationic defects in common, but the defect sites for Pr<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] are on different crystallographic positions as compared to Nd<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>], making both structures not completely isotypic.

If the volumes of the unit cells for Ce<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] ( $a = 680.57(5)$  pm,  $b = 2296.85(15)$  pm,  $c = 1172.26(8)$  pm,  $\beta = 124.096(1)^\circ$  for  $Z = 6$  at 100 K), Pr<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] (vide supra) and Nd<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] ( $a = 682.41(5)$  pm,  $b = 757.98(6)$  pm,  $c = 961.03(7)$  pm,  $\alpha = 90.176(3)^\circ$ ,  $\beta = 91.789(3)^\circ$ ,  $\gamma = 90.108(3)^\circ$  for  $Z = 2$  at 293 K) are compared and the effect of the lanthanoid contraction is taken into account, they can be nicely compared, if the number of formula units in the unit cell is reduced to  $Z = 2$ . Then the volumes are 0.506 nm<sup>3</sup> for Ce<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>], 0.501 nm<sup>3</sup> for Pr<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] and 0.497 nm<sup>3</sup> for Nd<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>].



**Figure 1.** Extended unit cell of Pr<sub>1.333</sub>[P<sub>2</sub>Se<sub>6</sub>] with shown P–P and P–Se bonds to illustrate the isolation of the complex [P<sub>2</sub>Se<sub>6</sub>]<sup>4-</sup> anions (mid) and bicapped trigonal prisms [PrSe<sub>8</sub>]<sup>13-</sup> for Pr1 (left) and the defect site Pr2 (right) shown as tritocircles in the mid.

[1] J. A. Aitken, M. Evain, L. Iordanis, M. G. Kanatzidis, (2002) *Inorg. Chem.* **41**, 180.

[2] B. M. Schulz, *Neues über Chalkogenophosphate mit Alkali- und Seltenerdmetallen*. Dissertation (2020), Universität Stuttgart.

[3] M. V. Kurz, B. M. Schulz, Th. Schleid, (2020) *Z. Kristallogr.* **S40**, 63.

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