Poster

$Pr_3OI[AsO_3]_2$: The First Oxide Iodide Oxoarsenate of the Rare-Earth Metals

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In analogy to the *non*-centrosymmetric $Ln_3OX[AsO_3]_2$ representatives (*Ln* = Ce – Nd, Sm – Dy; *X* = Cl and Br)[1–5], the isostructural iodide $Pr_3OI[AsO_3]_2$ was obtained in synthetic experiments with Pr, PrI_3, As_2O_3 with CsI as flux by means of a partial metallothermic reduction at 850 °C. The green, needle-shaped crystals could be recovered phase-pure after removal of the resulting monolithic arsenic crystal. $Pr_3OI[AsO_3]_2$ crystallizes in the tetragonal space group $P4_2nm$ with the lattice parameters a = 1289.13(9) pm, c = 559.24(5) pm and c/a = 0.434 for Z = 4 (CSD-2306280). The crystal structure contains two positions for the Pr^{3+} cations (Pr1 at 4*c*: 0.24148(8), 0.24148(8), 0.0000(6) and Pr2 at 8*d*: 0.13722(9), 0.45738(9), 0.5286(7)), only one for I^- (I at 4*c*: 0.37891(12), 0.37891(12), 0.4725(5)) and As^{3+} (As at 8*d*: 0.03472(15), 0.21332(15), 0.4988(7)) as well as four O^{2-}-anion sites (O1 at 4*b*: 0, ½, 0.261(5); O2 at 8*d*: 0.2113(12), 0.4201(12), 0.966(4); O3 at 8*d*: 0.0961(13), 0.2768(13), 0.746(3); O4 at 8*d*: 0.0949(14), 0.2916(14), 0.275(3)). $(Pr1)^{3+}$ is surrounded sixfold by O^{2-} anions forming trigonal prisms, which are capped by an I^- anion each ($[(Pr1)O_6I]^{10-}$), whereas $(Pr2)^{3+}$ has also one I^-, but seven O^{2-} anions as coordination sphere resulting in bicapped trigonal prisms $[(Pr2)O_7I]^{12-}$ (Figure 1). These $[(Pr2)O_7I]^{12-}$ polyhedra are stacked alternatingly along [001] to form columns and edge-linked with $[(Pr1)O_6I]^{10-}$ polyhedra, which alternate with each other and form rings parallel to the (001) plane. The *non*-bonding electron pairs at the ψ^1-tetrahedral $[AsO_3]^{3-}$ anions point into cavities, which run along [001] (Figure 2), as do the chains of *trans*-edge shared $[(O1)Pr_4]^{10+}$ tetrahedra.

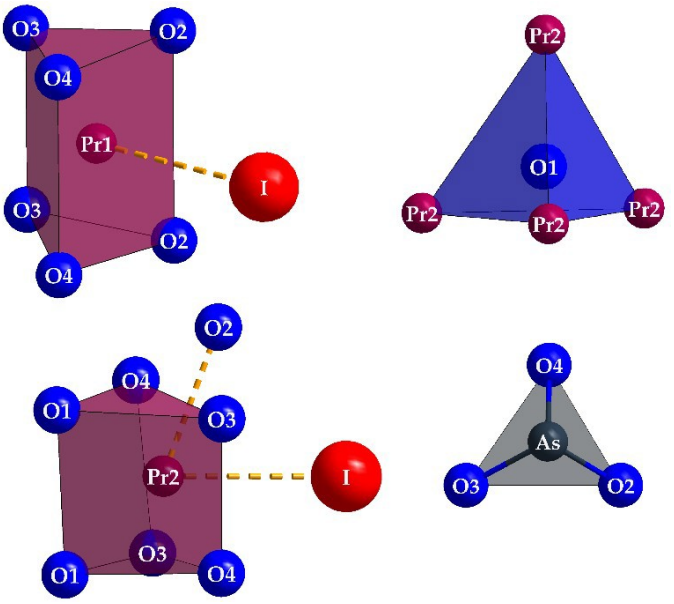

Figure 1. Capped and bicapped trigonal prisms $[(Pr1)O_6I]^{10-}$ and $[(Pr2)O_7I]^{12-}$ (*left*) as well as $[OPr_4]^{10+}$ tetrahedron and ψ^1-tetrahedral $[AsO_3]^{3-}$ anion (*right*) in the crystal structure of $Pr_3OI[AsO_3]_2$.

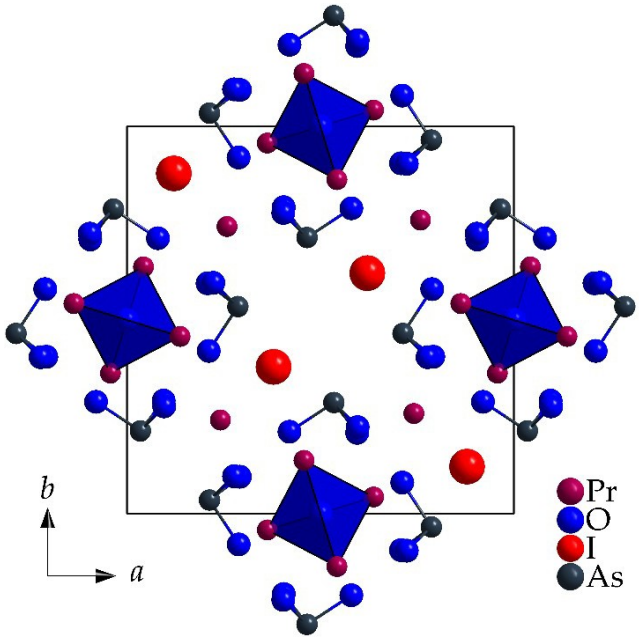

Figure 2. View at the tetragonal crystal structure of $Pr_3OI[AsO_3]_2$ along [001].

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