MS15-2-8 $Rb_2I_8Nd_4Sb_{16,667}O_{28}$: A Quinary Oxoantimonate(III) Iodide with Rubidium and Neodymium
#MS15-2-8

R.J.C. Locke [1], K.N. Bozenhardt [1], T. Schleid [1]
[1]University of Stuttgart - Stuttgart (Germany)

Abstract
In attempts to synthesize $NdSb_2O_4I$ in analogy to $NdBi_2O_4I$[1], with $Rb_2I_8Nd_4Sb_{16.667}O_{28}$ the first flux-containing rare-earth metal(III) oxoantimonate(III) iodide could be obtained via solid-state reactions, which forms pale violet, long thin, needle-shaped crystals. It crystallizes in the monoclinic space group *C*2/*m* with *a* = 2269.98(17) pm, *b* = 415.27(3) pm, *c* = 1284.56(9) pm and β = 96.559(3)° for *Z* = 1 (CSD-2169526).
Four out of five crystallographically distinct Sb^{3+} cations (Sb1–Sb4) form square ψ^1-pyramids $[SbO_4]^{5-}$ (Figure 1, *right*) together with four oxygen atoms and a stereochemically active non-bonding electron pair each. These pyramids exhibit Sb^{3+}–O^{2-} distances from 196 to 228 pm and are linked either by two edges or by two edges and one corner. The fifth Sb^{3+} cation (Sb5) forms rather a ψ^1-tetrahedron $[SbO_3]^{3-}$ (Figure 1, *right*) with only three oxygen atoms at similar distances and its lone pair. There is some disorder present, which causes to be the Sb4 and Sb5 positions only partially occupied. In this new structure, for the first time, a triple and a quadruple coordination mode of the Sb^{3+} cations with oxygen atoms occurs simultaneously. The ψ^1-pyramids are each linked by edges, while the ψ^1-tetrahedra are connected by corners, resulting in infinite strands of so-called “halfpipes” (Figure 1, *left*) propagating along [010].
The structure displays $[NdO_8]^{13-}$ hemiprisms, which share by four skew edges to form a kind of staircase structure. These polyhedra are located within antimony-oxygen “halfpipes” with each oxygen atom of a hemiprism also belonging to the “halfpipe”. The Rb^+ cations, occupying only one half of their crystallographic positions, have six iodide anions as neighbours to form trigonal prisms $[RbI_6]^{5-}$, which share two trans-oriented faces to form endless chains according to 1D-$\{[RbI^f_{6/2}]^{2-}\}$ (Figure 2).

References
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[2] R. J. C. Locke, *Doctoral Dissertation* **2024**, University of Stuttgart, *in preparation.*
[3] K.-N. Bozenhardt, *Master Thesis* **2022**, University of Stuttgart.

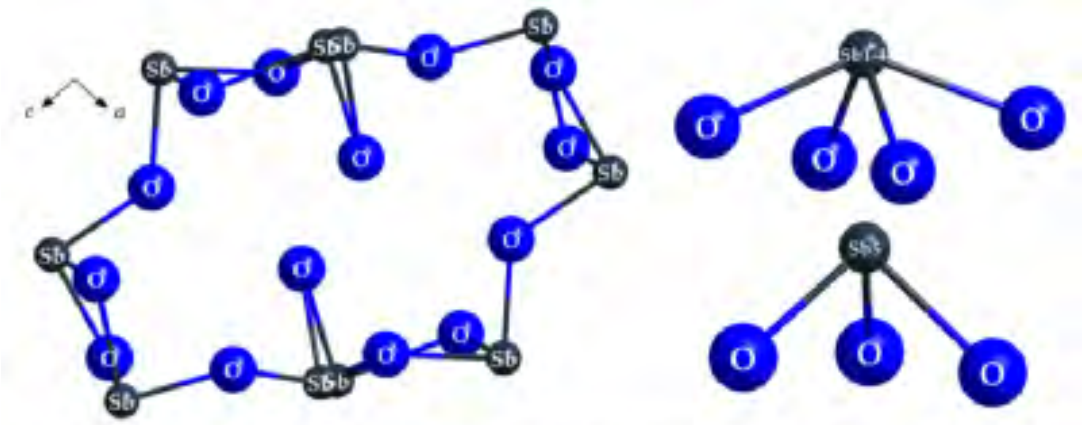

Figure 1. Antimony-oxygen "halfpipes" (*left*) and their building blocks (ψ^1-pyramids $[(Sb1–4)O_4]^{5-}$ and ψ^1-tetrahedra $[(Sb5)O_3]^{3-}$, *right*).

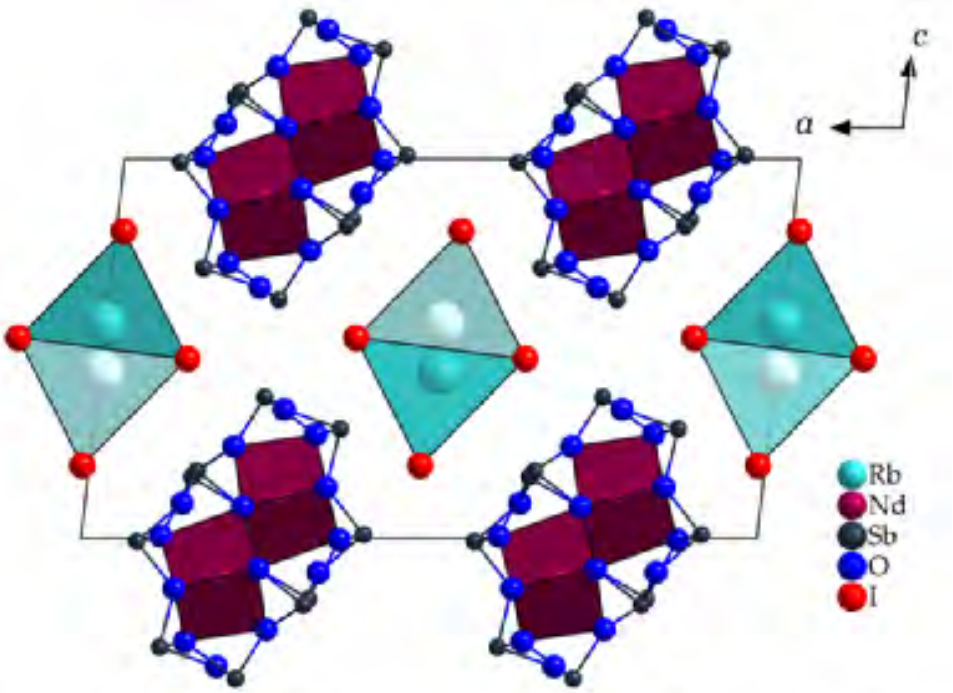

Figure 2. Projection of the monoclinic crystal structure of $Rb_2I_8Nd_4Sb_{16.667}O_{28}$ onto [010] emphasizing the antimony-oxygen "halfpipes" filled with $[NdO_8]^{13-}$ polyhedra.