MS15-1-11 Oxometallates A_3MO_2 with linear anions
#MS15-1-11

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Abstract
A series of oxometallates A_3MO_2 (*A* = Na, K, Rb, Cs; *M* = Fe, Co, Ni, Cu, Ag, Au) with linear anions $[O–M^{I}– O]^{3–}$ have been characterised [1-6]. Their respective crystal structures have been described in multiple ways, complicating a comprehensive overview for this family of oxometallates. We present three new compounds and propose an overarching description on the basis of the structural relations of the cation packings in the majority of A_3MO_2 oxometallates to an idealised α-Uranium packing.
Dark red Cs_3NiO_2 crystals were prepared from NiO, Cs and Cs_2O at 250 °C in a closed tantalum crucible. It crystallises in the Cs_3AuO_2 structure type [1] (*P*2_1/*c*, *Z* = 12, *a* = 10.076(2) Å, *b* = 19.557(2) Å, *c* = 13.881(2) Å, β = 132.730(14)°, *V* = 2009.4(5) Å^3), in contrast to the reported modification described in *P*4_2/*mnm* obtained by azide-nitrate route [2].
Yellow crystals of Cs_3CuO_2 were obtained in two modifications under similar synthesis conditions and were prepared from Cu metal and Cs_2O in closed silver or tantalum crucibles. One modification of Cs_3CuO_2 also adopts the Cs_3AuO_2 structure type [1] (*P*2_1/*c*, *Z* = 12, *a* = 10.0221(3) Å, *b* = 19.5023(5) Å, *c* = 13.8005(3) Å, β = 132.5160(10)°, *V* = 1988.19(9) Å^3). The other modification crystallises in a new structure type (*P*-1, *Z* = 6, *a* = 10.0322(10) Å, *b* = 10.0154(9) Å, *c* = 10.2089(8) Å, α = 93.815(4)°, β = 103.273(5)°, γ = 90.417(5)°, *V* = 995.8(2) Å^3).
The figure below shows various features of the Cs_3NiO_2 crystal structure. Constrictions of the linear $[NiO_2]^{3-}$ anions result in a particular sequence of edge and corner sharing distorted $[O(Cs_5Ni)]$ octahedra (red). These octahedral voids connect distorted hexagonal nets from both Cs and Ni atoms (blue and green, respectively). Atoms of one layer sit on top of the edge of triangles of an adjacent layer, giving an idealised α-U packing. Therefore, Cs_3NiO_2 can be described as *ADA'D'A''D''* sequence of Cs+Ni layers with ½ of the octahedral voids occupied by O. The structural analogies can be found in almost all representatives of this class of oxometallates and become even more striking for those compounds with higher symmetry.
Starting from an idealised α-Uranium structure (*I*4/*mmm*, experimental α-Uranium structure in *Cmcm* [7]), the A_3MO_2 structure family and occurring phase transitions can be described in a comprehensive way and, to some extent, be rationalised in a Bärnighausen tree.

References
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