$Ce_2[MoO_5][MoO_4]$ and $Ce_5[MoO_4]_8$: Two New Cerium Oxomolybdates, Each Exhibiting a Special Structural Feature

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$Ce_2[MoO_5][MoO_4]$ crystallizes monoclinically in space group $P2_1/c$ (a = 2241.98(9), b = 712.95(3), c = 2044.19(8) pm, β = 116.936(2)°, Z = 16). Besides eight crystallographically different Ce^{3+} cations with coordination numbers ranging from seven *plus* one to ten, its structure contains two isolated oxomolybdate(VI) species, namely $[MoO_4]^{2-}$ tetrahedra and $[MoO_5]^{4-}$ trigonal bipyramids and square pyramids. The oxygen polyhedra around the Ce^{3+} cations build up a three-dimensional $^3_\infty\{[Ce_2O_9]^{12-}\}$ network by vertex-, edge-, and face-connections with the Mo^{6+} cations residing in tetrahedral, square-pyramidal, and trigonal-bipyramidal voids therein. $Ce_5[MoO_4]_8$ also crystallizes monoclinically in space group $P2_1/c$ (a = 1133.14(5), b = 1704.96(7), c = 1406.21(6) pm, β = 90.749(2)°, Z = 4). In its structure eight isolated $[MoO_4]^{2-}$ tetrahedra are present, which display an overall negative charge of −16. To maintain electroneutrality, mixed-valency of the five crystallographically independent cerium cations must be considered. A thorough bond-valence analysis reveals cerium at the Ce1 site as tetravalent, while the other four cerium cations prove to be trivalent. The polyhedra around all cerium cations form chains with a V-shaped profile along [100] *via* vertex-, edge-, and face-connections to result in a sawblade pattern. These chains are interlocked into sheets parallel to the (001) plane and linked by the Mo^{6+} cations to form a three-dimensional network.

Key words: Cerium, Oxomolybdates, Crystal Structure, Mixed Valency