CsCu$_3$Dy$_2$S$_5$ and CsCu$_3$Er$_2$S$_5$: Two Isotypic Quaternary Sulfides of the Lanthanides with Channel Structures
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Orthorhombic single crystals of CsCu$_3$Dy$_2$S$_5$ ($a = 397.54(4)$, $b = 1414.8(1)$, $c = 1685.7(2)$ pm) and CsCu$_3$Er$_2$S$_5$ ($a = 394.82(4)$, $b = 1410.9(1)$, $c = 1667.2(2)$ pm; both Cmcm, $Z = 4$) are obtained as by-products (pale yellow or pink transparent needles) in attempts to synthesize CuMS$_2$ ($M =$ Dy and Er) through the oxidation of elemental copper, dysprosium and erbium, respectively, with sulfur (molar ratios: 1:1:2) in the presence of equimolar amounts of cesium chloride (CsCl) as fluxing agent at 900°C within fourteen days from torch-sealed evacuated silica tubes. Their crystal structure contains octahedral [MS$_6$]$^{9-}$ units ($d$(M-S) = 269 - 282 pm) which share edges and vertices to form layers $\frac{2}{3}${(M$_2$S$_5$)}$^{4-}$ parallel (010). These are three-dimensionally interconnected along [010] by two crystallographically different Cu$^+$ cations in tetrahedral coordination of S$_2^{2-}$ anions ($d$(Cu-S) = 227 - 269 pm) according to $\frac{3}{5}${(Cu$_3$M$_2$S$_5$)$_{12}$}. Thereby a likewise layered substructure $\frac{2}{3}${(Cu$_3$S$_5$)$_{12}$} is formed parallel (010) by edge- and vertex-linking of all [CuS$_4$]$^{7-}$ tetrahedra. Large channels within the $\frac{3}{5}${(Cu$_3$M$_2$S$_5$)} network spread along [100] and suit well to take up the highly coordinated Cs$^+$ cations, which are surrounded by eight plus one S$_2^{2-}$ anions at distances between 340 and 358 pm ($8\times$) with the ninth ligand 420 - 421 pm apart in the shape of (2+1)-fold capped trigonal prisms.