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NEW Ag(II)- AND Au(III)-FLUORIDES

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Single crystals of dark blue violet $\text{Ag}_3\text{M}_2^{\text{IV}}\text{F}_{14}$ ($\text{M}^{\text{IV}} = \text{Zr, Hf}$) has been obtained by heating mixtures of $\text{Ag}_2\text{O} + \text{ZrO}_2$ (HfO_2) under F_2 (little diluted by N_2) of about 600°C for 5-6 weeks. $\text{Ag}_3\text{Hf}_2\text{F}_{14}$ ($\text{Ag}_3\text{Zr}_2\text{F}_{14}$) crystallizes monoclinic ($\text{C}2-\text{C}_2^3$, No.5, $Z=2$) with $a=9.249$, $b=6.686$, $c=9.073 \text{ \AA}$, $\beta=90.26^\circ$. There are two different sorts of Ag^{2+} , one ($\text{Ag}[1]$) with C.N. (Ag^{2+}) = 6 (4+2, distorted octahedron, $d_{\text{Ag-F}}=2.106(4x)$ and $2.319 \text{ \AA}(2x)$) and the other one ($\text{Ag}[2]$) with C.N. (Ag^{2+}) = 4 (nearly planar-quadratically, $d_{\text{Ag-F}}=1.994, 2.076, 2.105, 2.210 \text{ \AA}$, but with four F^- in $d_{(\text{Ag-F})}=2.478-2.906 \text{ \AA}$). $\text{Ag}[1]$ can be substituted by $\text{M}^{\text{II}} = \text{Cu, Zn, Ni, Mg}$, the isotypic compounds are purple violet, $\text{Ag}[2]$ by $\text{M}^{\text{II}} = \text{Ca, Cd, Hg}$, all intensively green.

Complexes Au(III)-fluorides are prepared by heating mixtures of suitable compounds of divalent or trivalent metals with gold (powder) under F_2/N_2 of about 350°C for 3-4 days. For growing single crystals so obtained powders has been heated in sealed gold tubes (filled under dry Ar) for 3-4 weeks of about $560-600^\circ\text{C}$. $\text{Me}(\text{AuF}_4)_2$ ($\text{Me} = \text{Zn, Ni, Mg}$), yellow, crystallizes monoclinic ($\text{P}2_1/\text{c}-\text{C}_{2h}^5$, No.14, $Z=2$), with $a=5.487$, $b=5.519$, $c=10.381 \text{ \AA}$, $\beta=109.26^\circ$ ($\text{M}^{\text{II}} = \text{Zn}$), $\text{Ba}(\text{AuF}_4)_2$, yellow, tetragonal ($\text{I}\bar{4}-\text{S}_4^2$, No.82, $Z=4$) $a=9.788$, $c=7.600 \text{ \AA}$. $\text{FCu}(\text{AuF}_4)$, yellow, crystallizes triclinic ($\text{P}\bar{1}-\text{C}_1^1$, No.2, $Z=1$) with $a=5.536$, $b=4.979$, $c=3.707 \text{ \AA}$, $\alpha=107.6^\circ$, $\beta=98.8^\circ$, $\gamma=89.6^\circ$. The coordination of Cu^{2+} is rather unusual: $d_{\text{Cu-F}}=1.853(2x), 2.029(2x), 2.205(2x)$. With MF_3 ($\text{M} = \text{In, La-Dy}$), compounds $\text{FM}_2(\text{AuF}_4)_5$, all yellow, tetragonal ($\text{P}4_12_12-\text{D}_4^4$, No.92, $Z=4$) with $a=8.369$, $c=25.998 \text{ \AA}$ ($\text{M}^{\text{III}} = \text{In}$) are obtained.