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NEW Pd(II) FLUORIDES

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Single crystals of $CsPd_2F_5$ (orange-brown, Imma-D_{2h}^{28}, No. 74; Z = 2; a = 6.53_3, b = 7.86_2, c = 10.79 Å) have been obtained (instead of '$CsPdF_3$') by heating mixtures of CsF and PdF_2 (ratio 1:1) in sealed gold tubes (under dry Ar) up to t ≈ 600°C (20-30 d). The structure is related closely to the $CsAgFeF_6$-type of structure [1], but, because of the 'absence' of one F^-, one half of the Pd^{2+}-ions is coordinated planar quadratically, the other half octehedrally. From Guinier data are isotypic $Me^{I}Pd_2F_5$ (Me^{I} = K, Rb, Tl), brown and $CsMe^{II}PdF_5$ (Me^{II} = Zn, Cd, Ni, Co, Mg), brown or yellow.

Under similar conditions single crystals of Rb_3PdF_5 (yellow, P4/mbm-D_{4h}^{5}, No. 127; Z = 2, a = 7.46_7, c = 6.49_7 Å) have been obtained (instead of 'Rb_2PdF_4') by heating mixtures of RbF and PdF_2 (ratio 2:1) in sealed gold tubes (under dry Ar) up to t ≈ 560°C (20-30 d). The coordinationnumber of Pd^{2+} is C.N. = 4 (planar quadratic). Isotypic are (single crystal data) Cs_3PdF_5, Rb_2CsPdF_5 (with ordered distribution of Rb, Cs) and K_3PdF_5, all yellow.

1 Bernd G. Müller, Journal of Fluorine Chemistry, 17, 317-329 (1981)

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BINUCLEAR AND HETEROBINUCLEAR FLUOROOXO COMPLEXES OF VANADIUM AND MOLYBDENUM WITH THE $Cs_3Fe_2F_9$ STRUCTURE

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$Cs_3Mo_2O_6F_3$, $Cs_3V_2O_4F_5$ and $Cs_3V_2O_2F_7$ crystallize in the hexagonal $Cs_3Fe_2F_9$ structure. The structure can be described in terms of close packed $Cs(O,F)_3$ layers, where the octahedral sites in two adjacent layers are filled with the transition metal ions, so forming face shared bioctahedral $M_2(O,F)_9$ units. Single crystal X-ray data are unable to distinguish between fluorine and oxygen atoms. Therefore no information can be obtained, whether oxygen or fluorine atoms occupy terminal or bridging positions in the $M_2(O,F)_9$ units. Infrared and Raman spectra of these compounds, however, prove that oxygen and fluorine atoms are randomly distributed over all layers in $Cs_3Mo_2O_6F_3$ and in $Cs_3V_2O_4F_5$ leading to the predominant species $[O_2FMoO_2FMoO_2F]^{3-}$ and, by a random distribution of the vanadium atoms as well, to the fluorine bridged anion $[O_2FVF_3VO_2F]^{3-}$. $Cs_3V_2O_2F_7$ contains the anion $[OF_2VF_3VF_2O]^{3-}$ with a statistical distribution of the oxygen atoms over the terminal sites.

The compounds $Cs_3Mo_xV_{2-x}O_{x+4}F_{5-x}$ and $Cs_3Mo_xV_{2-x}O_{2+2x}F_{7-2x}$ containing hetero binuclear anions have also been prepared. In both substances the oxygen atoms occupy terminal and bridging positions.