

I-53

## NEW Pd(II) FLUORIDES

Bernd G. Müller

Inst. f. Anorg. u. Analyt. Chemie der JLU, Heinn.-Buff-Ring 58, Giessen (F.R.G.)

Single crystals of  $\text{CsPd}_2\text{F}_5$  (orange-brown,  $\text{Imma-D}_{2h}^{28}$ , No. 74;  $Z = 2$ ;  $a = 6.533$ ,  $b = 7.862$ ,  $c = 10.79$  Å) have been obtained (instead of 'CsPdF<sub>3</sub>') by heating mixtures of CsF and PdF<sub>2</sub> (ratio 1:1) in sealed gold tubes (under dry Ar) up to  $t \approx 600^\circ\text{C}$  (20-30 d). The structure is related closely to the  $\text{CsAgFeF}_6$ -type of structure [1], but, because of the 'absence' of one F<sup>-</sup>, one half of the Pd<sup>2+</sup>-ions is coordinated planar quadratically, the other half octahedrally. From Guinier data are isotypic  $\text{Me}^{\text{I}}\text{Pd}_2\text{F}_5$  ( $\text{Me}^{\text{I}} = \text{K}, \text{Rb}, \text{Tl}$ ), brown and  $\text{CsMe}^{\text{II}}\text{PdF}_5$  ( $\text{Me}^{\text{II}} = \text{Zn}, \text{Cd}, \text{Ni}, \text{Co}, \text{Mg}$ ), brown or yellow.

Under similar conditions single crystals of  $\text{Rb}_3\text{PdF}_5$  (yellow,  $\text{P4/mbm-D}_2^{5h}$ , No. 127;  $Z = 2$ ,  $a = 7.467$ ,  $c = 6.497$  Å) have been obtained (instead of 'Rb<sub>2</sub>PdF<sub>4</sub>') by heating mixtures of RbF and PdF<sub>2</sub> (ratio 2:1) in sealed gold tubes (under dry Ar) up to  $t \approx 560^\circ\text{C}$  (20-30 d). The coordination number of Pd<sup>2+</sup> is C.N. = 4 (planar quadratic). Isotypic are (single crystal data)  $\text{Cs}_3\text{PdF}_5$ ,  $\text{Rb}_2\text{CsPdF}_5$  (with ordered distribution of Rb, Cs) and  $\text{K}_3\text{PdF}_5$ , all yellow.

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

I-54

BINUCLEAR AND HETEROBINUCLEAR FLUOROORO COMPLEXES OF VANADIUM AND MOLYBDENUM WITH THE  $\text{Cs}_3\text{Fe}_2\text{F}_9$  STRUCTURE

Rainer Mattes and Harry Förster

Institute of Inorganic Chemistry, University of Muenster, 4400 Muenster (F.R.G.)

$\text{Cs}_3\text{Mo}_2\text{O}_6\text{F}_3$ ,  $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$  and  $\text{Cs}_3\text{V}_2\text{O}_2\text{F}_7$  crystallize in the hexagonal  $\text{Cs}_3\text{Fe}_2\text{F}_9$  structure. The structure can be described in terms of close packed  $\text{Cs}(\text{O},\text{F})_3$  layers, where the octahedral sites in two adjacent layers are filled with the transition metal ions, so forming face shared bioctahedral  $\text{M}_2(\text{O},\text{F})_9$  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  $\text{M}_2(\text{O},\text{F})_9$  units. Infrared and Raman spectra of these compounds, however, prove that oxygen and fluorine atoms are randomly distributed over all layers in  $\text{Cs}_3\text{Mo}_2\text{O}_6\text{F}_3$  and in  $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$  leading to the predominant species  $[\text{O}_2\text{FMo}_2\text{O}_2\text{F}]^{3-}$  and, by a random distribution of the vanadium atoms as well, to the fluorine bridged anion  $[\text{O}_2\text{FVF}_2\text{VO}_2\text{F}]^{3-}$ .  $\text{Cs}_3\text{V}_2\text{O}_2\text{F}_7$  contains the anion  $[\text{OF}_2\text{VF}_2\text{VF}_2\text{O}]^{3-}$  with a statistical distribution of the oxygen atoms over the terminal sites. The compounds  $\text{Cs}_3\text{Mo}_x\text{V}_{2-x}\text{O}_{x+4}\text{F}_{5-x}$  and  $\text{Cs}_3\text{Mo}_x\text{V}_{2-x}\text{O}_{2+2x}\text{F}_{7-2x}$  containing hetero binuclear anions have also been prepared. In both substances the oxygen atoms occupy terminal and bridging positions.