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Note

ON THE THERMAL DECOMPOSITION OF $K_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$($K_3[V_2O_2(O_2)_3F_3] \cdot 2H_2O \cdot HF$)

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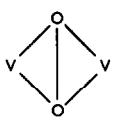
According to a previous study [1] $K_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$ decomposes in two stages. During the first stage water and hydrogen fluoride are released. The decomposition proceeds in the second step by the release of the peroxo oxygen. Results were interpreted without knowledge of the crystal structure.

The crystal structure of $K_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$ was recently solved [2] (cell parameters: $a = 0.8518(5)$, $b = 1.2460(5)$, $c = 0.5981(5)$ nm, $\alpha = 92.3(1)$, $\beta = 90.9(1)$, $\gamma = 102.7(1)°$, $Z = 2$, space group P_1). In accordance with the proposed structure [1,3], the anion contains the bridge



with a doubly bidentate peroxo group and the coordination number of the vanadium atom is seven (Fig. 1). But not all fluorine atoms are coordinated to vanadium atoms and the crystal structure contains molecules of hydrogen fluoride. The formula of the complex revealed by the structural analysis is $K_3[V_2O_2(O_2)_3F_3] \cdot 2H_2O \cdot HF$. It is therefore understandable why water and hydrogen fluoride are released almost simultaneously in the first stage of the decomposition. The whole decomposition process is described by the following equations:

$$K_3[V_2O_2(O_2)_3F_3] \cdot 2H_2O \cdot HF = K_3[V_2O_2(O_2)_3F_3] + 2H_2O + HF$$

$$K_3[V_2O_2(O_2)_3F_3] = KVO_3 + K_2[VO_2F_3] + 3/2O_2$$

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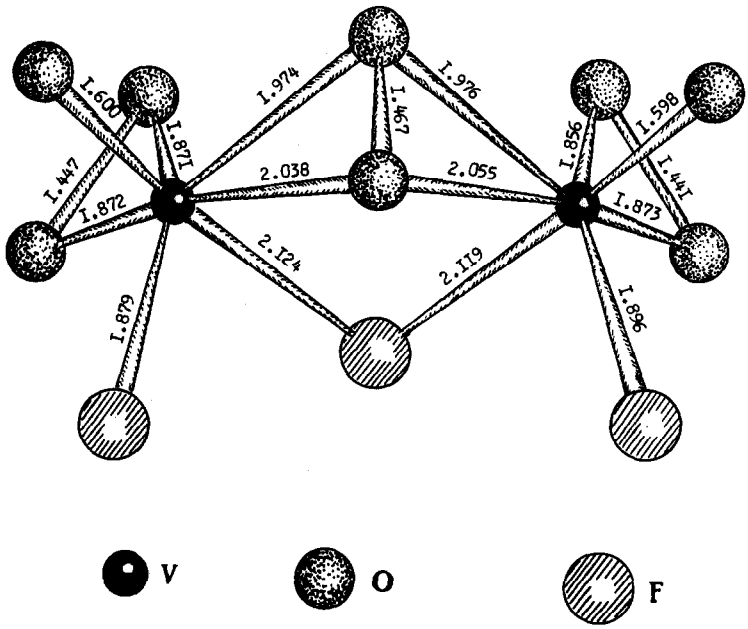

Fig. 1. The structure of the $[V_2O_2(O_2)_3F_3]^{3-}$ ion.

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