

SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION
OF THE HYDRAZINIUM(1+) COMPOUNDS $(N_2H_5)_6M_2F_{14}$ (M = Zr, Hf)

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Two new compounds of Zr(IV) and Hf(IV), $(N_2H_5)_6M_2F_{14}$, were synthesized from aqueous solutions of $(N_2H_6)_3M_2F_{13} \cdot F$ [1] and $N_2H_4 \cdot H_2O$. Vibrational spectra show a composite anion with a coordination number larger than 6 and two types of $N_2H_5^+$ cations involved predominantly through their NH_3^+ groups in weak H-bonds. On heating, both compounds go through a phase transition at 78 °C and then start losing weight above 120 °C (Zr-compound) or 110 °C (Hf-compound). The first step, transition from the $N_2H_5^+$ compound to $(NH_4)_2MF_6$ is accompanied by a strong exothermic effect with a DTA peak at 220 °C for Zr and at 205 °C for Hf compound. In the second step, 275 °C for Zr and 281 °C for Hf, NH_4MF_5 is obtained. The decomposition ends with MF_4 at 353 °C for Zr and at 378 °C for Hf. Intermediates were characterized by weight loss, chemical analysis, powder diffraction data and vibrational spectra. Raman spectra show that the anionic part of the compounds transforms during thermal decomposition through other composed fluorozirconate(IV) or hafnate(IV) anions to MF_4 , and that no octahedral MF_6^{2-} ion appears.

- 1 J. Slivnik, A. Šmalc, B. Sedej and M. Vilhar, Vestn.Slov.Kem.Drus., **11**, 53 (1964); J. Slivnik, B. Jerkovič and B. Sedej, Monatsh.Chem., **97**, 820 (1966).