

CRYSTAL STRUCTURE AND VIBRATIONAL SPECTRA OF THE  
HYDRAZINIUM(2+) COMPOUNDS  $(N_2H_6)_3M_2F_{13}\cdot F$  (M = Zr, Hf)

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$(N_2H_6)_3M_2F_{13}\cdot F$  are members of a series of hydrazinium(1+) and (2+) compounds of diverse composition, synthesized from aqueous solutions [1]. Their large molecular formula makes them structurally interesting. The Zr compound crystallizes in the space group  $P2_1$  (No. 4) ( $a = 5.670(1)$ ,  $b = 10.984(2)$ ,  $c = 10.601(2)$  Å,  $\beta = 93.88(1)^\circ$ ,  $V = 658.7(4)$  Å<sup>3</sup>,  $Z = 2$ ). Two different types of  $N_2H_6^{2+}$  ions are present. One is involved in strong H-bonds to  $F^-$  ions in chains running along the a-axis, and the other links the structure through H-bonds to fluorines of the  $Zr_2F_{13}^{5-}$  ions. The dimeric  $Zr_2F_{13}^{5-}$  ions, having very nearly  $C_2$  point symmetry, are of a kind yet unobserved in Zr-compounds [2]. They are formed by joining two distorted bicapped trigonal prisms of  $ZrF_8$ -units through a common face.  $(N_2H_6)_3Hf_2F_{13}\cdot F$  is isomorphous. The vibrational spectra of the two compounds are nearly identical, with the exception of a strong infrared band, which is assigned to a stretching mode of the anion with the moving central atom. The anionic part of the spectrum is simple, and in accordance with other dimeric and polymeric hafnates(IV) and zirconates(IV). The cationic part clearly shows two types of  $N_2H_6^{2+}$  ions. H-bonding is strongly present in the spectra.

- 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).
- 2 A.F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 5 th edition, 1986, p. 471-474.