ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2010, Vol. 55, No. 9, pp. 1339–1346. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © N.A. Didenko, K.A. Gaivoronskaya, E.I. Voit, A.V. Gerasimenko, V.Ya. Kavun, 2010, published in Zhurnal Neorganicheskoi Khimii, 2010, Vol. 55, No. 9, pp. 1420–1428.

SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Synthesis and Studies of Magnesium Hexafluorozirconates $MgZrF_6 \cdot nH_2O$ ($n = 5, 2, 0$)

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Received October 8, 2009

Abstract—Crystalline magnesium hexafluorozirconate $MgZrF_6 \cdot 5H_2O$ isostructural to $MnZrF_6 \cdot 5H_2O$, and having a chain-like structure, was synthesized and studied. According to thermogravimetry, the compound undergoes stepwise dehydration in the temperature range of 50–420°C to give the stable phase $MgZrF_6 \cdot 2H_2O$ and the final product $MgZrF_6$ isostructural to the cubic modification of $MZrF_6$ (M = Cu, Fe). The vibrational spectra of the initial compound and the dehydration products are analyzed and the structures of the compounds are considered.

DOI: 10.1134/S0036023610090020

Previously, we noted that replacement of one outer-sphere cation M in hexafluorozirconates M_2ZrF_6 by another single-charged cation M' results, most often, in the formation of compounds differing in the structure and in the mode and energy characteristics of ionic motions. Therefore, we synthesized a number of hexafluorozirconates with heteroatomic cationic sublattice (isovalent substitution) and studied their structure, the dynamics of complex ions, and electrophysical properties [1, 2]. Of obvious interest was the preparation and study of hexafluorozirconates with mixed cationic sublattice with heterovalent substitution, for example, substitution of a doubly charged cation for a singly charged one, which may bring about the necessity of charge compensation resulting in vacancies appearing in the structure.

To date, the structures of the compounds $K_2M^{II}(ZrF_6)_2 \cdot 6H_2O$ (M^{II} = Cu, Zn), in which the complex anions are dimers consisting of ZrF_6^{2-}, ions and the cationic sublattice is composed of $[M(H_2O)_6]^{2+}$ and K^+ ions, have been investigated [3, 4]. The difference between the ionic radii in the K^+–Zn^{2+} and K^+–Cu^{2+} pairs is about 40%. As the doubly charged cation, we chose Mg^{2+}, whose ionic radius is close to that of the Li^+ ion. Previously, magnesium hexafluorozirconate was synthesized and studied (as crystal hydrates and as the anhydrous salt) as the model object for solving problems concerning the crystal structure, the character of internal motion and phase transitions, thermal properties, and so on.

In the series of hexafluorozirconate salts with doubly charged cations, magnesium hexafluorozirconate has been scarcely studied so far: the structure of its crystal hydrates isolated from solutions has not been determined, the possibility or conditions of synthesis of anhydrous $MgZrF_6$ through its hydrates has not been elucidated. Previously [5], it was noted that Mg and Mn salts that crystallize from solutions contain five water molecules and are isostructural to each other.

The purpose of this work was to optimize the synthesis conditions for individual hydrates and anhydrous magnesium hexafluorozirconate, determine the phase composition, compare the thermal characteristics, and elucidate structurization features in the higher crystal hydrate–anhydrous compound series on the basis of IR and Raman spectroscopy data.

EXPERIMENTAL

Special purity grade ZrO_2, reagent grade $Mg(NO_3)_2 \cdot 6H_2O$, and special purity grade 40% HF were used. Magnesium hexafluorozirconate was prepared by slow dropwise addition of a solution of $Mg(NO_3)_2 \cdot 6H_2O$ to a stirred solution of ZrO_2 (concentration 1.6 mol/L) in 40% HF heated on a boiling water bath (component molar ratio 1 : 1). Precipitation took place immediately after mixing the reactants. The resulting salt was washed with acetone and dried in air. According to the results of chemical analysis, the precipitated phase was the crystal hydrate $MgZrF_6 \cdot 2H_2O$. According to powder X-ray diffraction, this product may contain magnesium fluoride as an impurity (precipitated due to poor solubility as a gel-like product responsible for a halo in the X-ray diffraction patterns). After the subsequent dissolution of the contaminated magnesium hexafluorozirconate precipitate in water, MgF_2 was separated by filtration, while slow evaporation of the filtrate at room temperature or in a refrigerator resulted in growth of large transparent colorless crystals of $MgZrF_6 \cdot 5H_2O$ (**I**) soluble in water and decaying on storage in air (metastable compound) to give

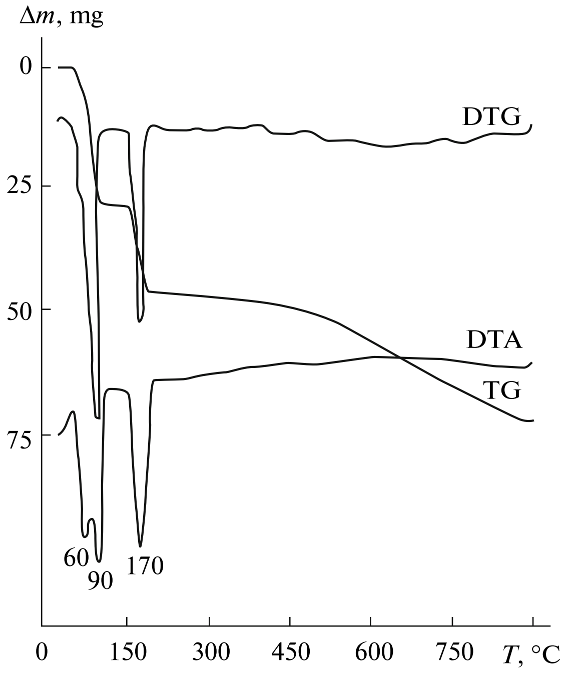

Fig. 1. Curves of heating of $MgZrF_6 \cdot 5H_2O$ in air.

dihydrate. Evaporation of the filtrate at $T > 50$°C gave a finely crystalline precipitate of $MgZrF_6 \cdot 2H_2O$ whose X-ray diffraction characteristics coincide with the characteristics for the same compound that crystallizes from hydrofluoric acid solutions. Unfortunately, we were unable to grow single crystals of the dihydrate for X-ray diffraction. We studied the starting magnesium hexafluorozirconate pentahydrate and the products of its thermal decomposition formed upon partial ($MgZrF_6 \cdot 2H_2O$) and complete ($MgZrF_6$) dehydration. The products of synthesis were identified by powder X-ray diffraction, IR and Raman spectroscopy, and chemical analysis using standard procedures.

For $MgZrF_6 \cdot 5H_2O$ anal. calcd. (%): Mg, 7.52; Zr, 28.53; F, 35.74; H_2O, 28.21.

Found (%): Mg, 7.45; Zr, 28.60; F, 36.35; H_2O, 27.6 (TG data).

The X-ray diffraction patterns of magnesium hexafluorozirconate and intermediate and final products of its thermal decomposition were recorded on Bruker D8 Advance (CuK_α radiation, graphite monochromator) and Stoe Stadi P diffractometers ($CuK_{\alpha 1}$ radiation, Ge monochromator).

The differential thermal analysis of magnesium hexafluorozirconate hydrates was carried out in undried air on a Q-1000 MOM derivatograph at sample heating rates of 2.5 and 5 K/min. The sample weight was 170 mg. Calcined Al_2O_3 was used as the reference.

IR spectra of the samples at 100–4000 cm^{-1} were recorded on a Shimadzu FTIR Prestige-21 and Bruker Vertex-70 FT IR spectrometers with a resolution of 2 cm^{-1}. Raman spectra were obtained with a 2 cm^{-1} resolution in the backscattering mode on a Bruker RFS100/S spectrometer (Nd:YAG laser, $\lambda = 1064$ nm, 50 mW).

In this study, the principal bands in the vibrational spectra of $MgZrF_6 \cdot 5H_2O$, $MgZrF_6 \cdot 2H_2O$, and $MgZrF_6$ were assigned on the basis of quantum-chemical calculations and published data. The quantum-chemical calculations were carried out using the Gamess program package [6], by local density functional theory method in the 321G basis set for all atoms [7–9] using the B3LYP exchange-correlation potential [10]. All calculations were carried out on a 16-processor Linux cluster at the Institute of Chemistry (Far East Division, Russian Academy of Sciences).

RESULTS AND DISCUSSION

According to powder X-ray diffraction data, the synthesized $MgZrF_6 \cdot 5H_2O$ was isostructural to $MnZrF_6 \cdot 5H_2O$ [11, 12] with the parameters a = 15.5100(4) Å, b = 7.4733(2) Å, c = 8.8484(2) Å, β = 124.043(1)°; space group $C2$. The structure of the latter was composed of chains of edge-sharing ZrF_8 dodecahedra reinforced with $MnF_2(H_2O)_4$ octahedra and uncoordinated water molecules. Later, monoclinic crystals of $ZnZrF_6 \cdot 5H_2O$, also isostructural to analogous manganese salt, were obtained [13].

The isostructural nature of $MZrF_6 \cdot 5H_2O$ (M = Mn, Mg, Zn) implies the same type of thermal behavior. According to published data [14], dehydration of manganese hexafluorozirconate pentahydrate occurs stepwise with successive elimination of four water molecules (in the temperature range of 80–220°C) and one water molecule (220–250°C) (recording under inert atmosphere) and dehydration of similar zinc salt occurs at 100–112, 123–162, and 186–194°C with elimination of totally 4.7 H_2O molecules. In the 228–396°C range, the components being removed are H_2O and HF (recording in air) [13].

The results of thermoanalytical studies of compound $MgZrF_6 \cdot 5H_2O$ are presented in Fig. 1. As can be seen from the derivatogram of magnesium hexafluorozirconate pentahydrate, during heating in the temperature range of 50–250°C, the DTA curve shows three endotherms with maxima at 60, 90, and 170°C reflecting the stepwise dehydration. A comparison of the position of the maximum at 60°C and the weight loss curve (in the temperature range of 50–60°C, the weight loss was 5–6%, no step in the TG curve was present) leads to the conclusion that the first endotherm corresponds to incongruent melting of the initial salt. The incongruent melting of the crystal hydrates involves the formation and growth of the nuclei of the solid phase of the product with inclusion of liquid solution [15]. We analyzed the products obtained on heating of $MgZrF_6 \cdot 5H_2O$ in a derivatograph at a rate of 2.5 K/min to 55 and 65°C. Both samples were moist thick pulps that dried in air. According to X-ray diffraction, the product heated to 55°C consisted of a mixture of $MgZrF_6 \cdot 5H_2O$ and $MgZrF_6 \cdot 2H_2O$, while the product heated to 65°C was a single phase, $MgZrF_6 \cdot 2H_2O$. The endotherm at 90°C in the thermogram of $MgZrF_6 \cdot 5H_2O$ is related to evaporation of the moisture liberated during the incongruent melting of the pentahydrate. The weight loss (Δm_{exp}) at 120–130°C was 16.7%, which corresponds to the removal of three water molecules from compound I Δm_{calcd} = 16.93%) to give $MgZrF_6 \cdot 2H_2O$. After heating to 130°C, the sample was no longer friable but was an agglutinated material coated with a crust. The X-ray diffraction pattern of this compound was indexed in the orthorhombic system with parameters of a C-centered unit cell: $a = 7.171(1)$ Å, $b = 11.245(2)$ Å, $c = 7.391(2)$ Å; space group *Cccm*. Proceeding from the structure of $MgZrF_6 \cdot 5H_2O$, one can assume that, on heating this compound, the uncoordinated water molecule should be the first to be eliminated. The disruption of the hydrogen bond system results in a structural rearrangement with removal of two more water molecules from the magnesium coordination sphere to give the dihydrate. The endotherm in the range of 150–250°C corresponds to dehydration of $MgZrF_6 \cdot 2H_2O$ to give $MgZrF_6$ ($\Delta m_{exp} = 27.6\%$, $\Delta m_{calcd} = 28.21\%$). Thus, the endothermic processes occurring on heating $MgZrF_6 \cdot 5H_2O$ (to 250°C) can be represented by the following scheme:

$$MgZrF_6 \cdot 5H_2O_{solid} \xrightarrow{60} MgZrF_6 \cdot 2H_2O_{solid} + \text{liquid phase} + xH_2O_{vapor}$$

$$\xrightarrow{90} MgZrF_6 \cdot 2H_2O_{solid} + (3 - x)H_2O_{vapor},$$

$$MgZrF_6 \cdot 2H_2O_{solid} \xrightarrow{170} MgZrF_{6\ solid} + 2H_2O_{vapor}.$$

It was found that $MgZrF_6$ (obtained at 250°C) contacting with saturated water vapor at room temperature gradually passes to the dihydrate. Magnesium hexafluorozirconate is almost stable up to 420–430°C in a moist air atmosphere. The X-ray diffraction patterns of the products obtained by heating the pentahydrate to 250 and 420°C, respectively, are identical except for minor differences in the interplanar spacing. According to powder diffraction data, the compound $MgZrF_6$ refers to the ReO_3 type and is isostructural to the cubic modification of $MZrF_6$ (M = Cu, Fe) [16, 17]: space group $Fm\bar{3}m$ with the parameter $a = 7.933(1)$ Å.

According to thermal analysis data for $MgZrF_6 \cdot 5H_2O$ (Fig. 1), a slight (about 1%) weight loss takes place in the temperature range of 250–420°C. This can be related to the removal of residual water (the IR spectrum of the sample heated to 250°C exhibits weak bands for water vibrations) and/or to a minor degree of pyrohydrolysis of $MgZrF_6$. At higher temperatures (above 420–430°C), the weight gradually decreases but no clear-cut events are present in the DTA curve. This is due to hydrolytic decomposition of magnesium hexafluorozirconate. The high-temperature hydrolysis of $MgZrF_6$ involves the cation and corresponds to the acidic type according to the equation

$$MgZrF_6 + 2H_2O \longrightarrow Mg(OH)_2 + ZrF_4$$

$$+ 2HF \longrightarrow MgF_2 + ZrO_2 + 4HF.$$

The evolved HF fluorinates $Mg(OH)_2$ (or MgO) to give MgF_2, and pyrohydrolysis of ZrF_4 yields ZrO_2. According to powder X-ray diffraction, the sample obtained at 650°C is a mixture of $MgZrF_6$, MgF_2, and ZrO_2 phases, while, at 800–900°C, a binary mixture of MgF_2 and monoclinic ZrO_2 is formed. The rate of pyrohydrolysis of MgF_2 increases after decomposition of $MgZrF_6$ has been completed. Isothermal heating of the product representing a mixture of ZrO_2 and MgF_2 in a muffle furnace at 950°C for 1–2 h yielded a binary mixture of zirconium and magnesium oxides.

Thus, according to thermal analysis data, single-type compounds $MZrF_6 \cdot 5H_2O$ (M = Mn, Mg, Zn) are more stable (have higher dehydration temperature) with *d* transition element cations than with Mg^{2+}, although the radius of the latter is smaller than the radius of any of transition metal ions with the charge +2. Apparently, this is related not only to the cation radius but also to its polarizing action on the anion and water molecules. For equal charge and similar radius (all other factors being the same), the susceptibility for hydrolysis should be higher for $MZrF_6$ salts of cations with 18-electron (Zn^{2+}) and vacant (Mn^{2+}) shells than for a similar salt of an 8-electron cation (Mg^{2+}).

Certain trends in the structure formation in the higher crystal hydrate $MgZrF_6 \cdot 5H_2O$– anhydrous salt system can be followed from the IR and Raman spectroscopy data.

Vibrational spectra of $MgZrF_6$. Since $MgZrF_6$ is isostructural to $FeZrF_6$ [17], the main fragments of the crystal lattice of MgF_6 are MgF_6 and ZrF_6 polyhedra combined into a three-dimensional framework by linear Mg–F–Zr bridges. The high-frequency position of the $\nu_1(A_{1g})$ line in the Raman spectrum of $MgZrF_6$ and the number of bands correspond to the octahedral structure of the complex anion $[ZrF_6]^{2-}$.

In the quantum-chemical calculations, an isolated $[ZrF_6]^{2-}$ anion (O_h point group of symmetry) was taken as the model fragment of the lattice (Fig. 2a). The calculated optimal Zr–F distance (2.00 Å) for the ZrF_6^{2-} ion is in good agreement with the corresponding distance of 1.991(2) Å for structurally characterized $FeZrF_6$ (space group F*m*3*m*) [17].

Table 1 presents the calculated vibration frequencies of the $[ZrF_6]^{2-}$ anion and positions of the absorption maxima in the experimental vibrational spectra of magnesium hexafluorozirconate. The $[ZrF_6]^{2-}$ (O_h) vibrations are responsible for two IR bands: $\nu_3(T_{1u})$ (antisymmetric stretching mode ν_{as}(Zr–F)) and $\nu_4(T_{1u})$ (γ-ZrF_4 bending vibration). Three vibrations,

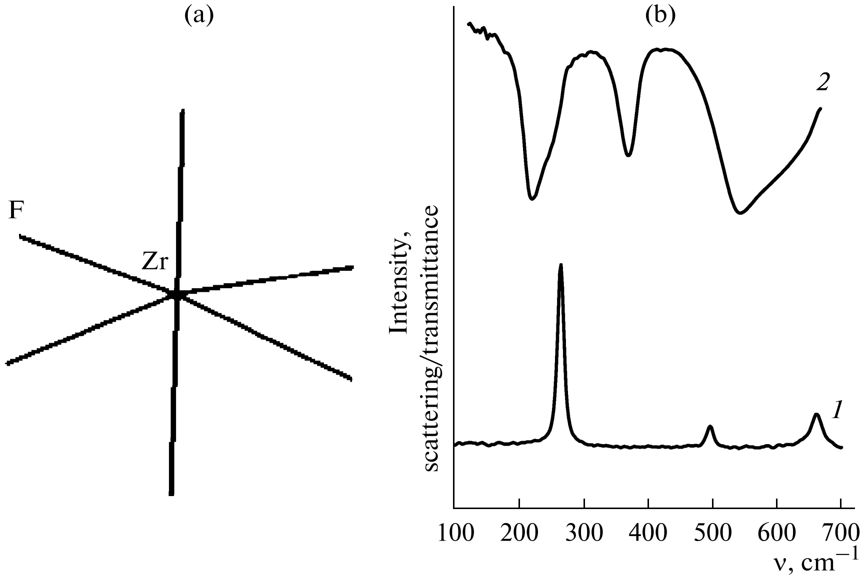

Fig. 2. (a) $[ZrF_6]^{2-}$ anion simulating the lattice of $MgZrF_6$; (b) (*1*) Raman and (*2*) IR spectra of $MgZrF_6$.

ν_1, ν_2, and ν_5 (A_{1g}, E_g, T_{2g}) are active in the Raman spectrum [18].

The band assignment in the vibrational spectrum of magnesium hexafluoride is in full agreement with published data [19, 20] concerning the assignment for $[ZrF_6]^{2-}$ ions in compounds A_2ZrF_6 (A = Li, K, Cs).

The IR spectrum of $MgZrF_6$ exhibits an additional intense band (369 cm^{-1}), which can be assigned only to the ν_{as}(Mg–F) stretches. No bands for MgF_6 vibrations were detected in the Raman spectrum, which can be attributed to a higher degree of ionicity of Mg–F bonds compared to the Zr–F bonds.

Vibrational spectra of $MgZrF_6 \cdot 5H_2O$. In view of the fact that $MgZrF_6 \cdot 5H_2O$ and $MnZrF_6 \cdot 5H_2O$ are isostructural, we assume that infinite anionic chains $[ZrF_6]_n^{2n-}$, formed from the dodecahedral ZrF_8 groups combined through two bridging fluorine atoms (F_b) are the main fragment of the lattice of $MgZrF_6 \cdot 5H_2O$. The interanionic space accommodates the $Mg(H_2O)_4^{2+}$ cations connected to the anion chain through two terminal fluorine atoms (F_t) (≈2.00 Å) (Fig. 3a). Thus, short Zr–F_t bonds (≈2.00 Å) and bridging Zr–F_b bonds (≈2.20 Å) can be distinguished in the compound structure (Fig. 3a, 3b).

The vibrational spectra were simulated using the model ion $[Zr_4F_{26}]^{10-}$ (D_{2h}) with fixed Zr atoms at the chain ends (Fig. 3b). The optimal Zr–F_t and Zr–F_b distances obtained in calculations (2.01, 2.21 Å) for two ZrF_8 groups connected by two F_b atoms (the central region of the fluorozirconate chain) are similar to the experimental distances found for the isostructural compound $MnZrF_6 \cdot 5H_2O$.

The vibrational spectra of crystal hydrates $MgZrF_6 \cdot nH_2O$ ($n = 2, 5$) can be conventionally divided into fre-

Table 1. Positions (cm^{-1}) of the absorption maxima in the spectra of $MgZrF_6$ and calculated vibration frequencies and band assignments for $[ZrF_6]^{2-}$ anion (O_h)

Experiment		DFT/321G calculation				Intensity	
ν, cm^{-1}		ν, cm^{-1}	assignment	symmetry		IR	raman
IR	raman						
	661	597	$\nu_s(ZrF_6)$	A_{1g}	ν_1	0.0	12.0
543		554	$\nu_{as}(ZrF_6)$	T_{1u}	ν_3	5.3	0.00
	496	500	$\nu_s(ZrF_2–ZrF_2)$	E_g	ν_2	0.0	4.7
369		–	–	–	–	–	–
	264	250	$\delta_{sciss}(ZrF_4)$	T_{2g}	ν_5	0.0	2.0
220		222	$\gamma(ZrF_4)$	T_{1u}	ν_4	0.6	0.0
		124	$\gamma(ZrF_2–ZrF_2)$	T_{2u}	ν_6	0.0	0.0

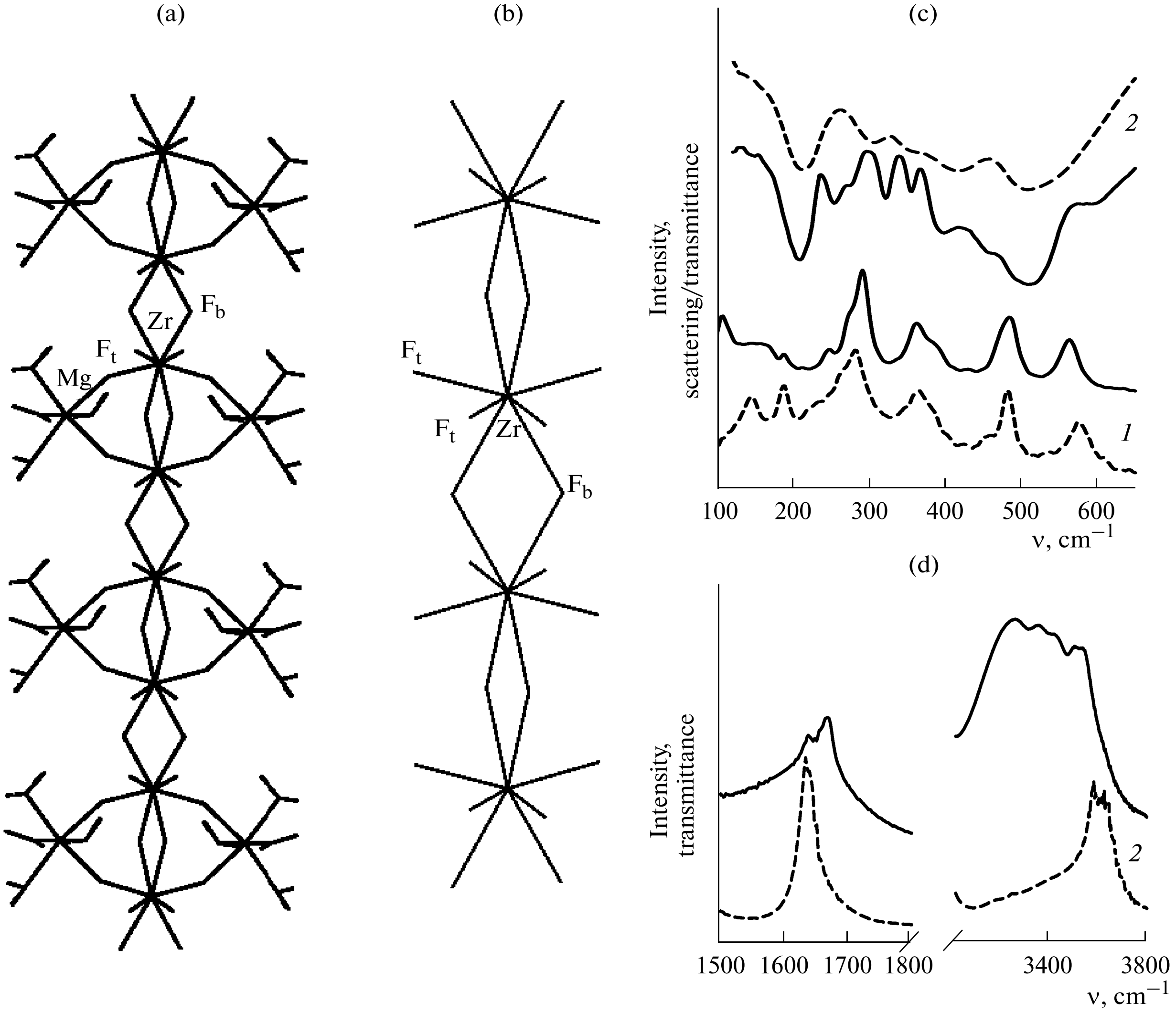

Fig. 3. (a) Fragment of the crystal lattice of $MgZrF_6 \cdot 5H_2O$; (b) model $[Zr_4F_{26}]^{10-}$ anion; (c, d) (*1*) Raman and (*2*) IR spectra of $MgZrF_6 \cdot 5H_2O$ (continuous line) and $MgZrF_6 \cdot 2H_2O$ (dashed line).

quency ranges. The 600–100 cm^{-1} range covers the stretching and bending vibrations of the fluorozirconate chain and Mg^{2+}-formed group (Fig. 3c), and the 3700–3000 and 1800–1500 cm^{-1} ranges correspond to the stretching and bending vibrations of the H_2O molecules (Fig. 3d).

Table 2 shows the band assignment and the calculated IR and Raman frequencies for the fluorozirconate anion $[Zr_4F_{26}]^{10-}$ (Fig. 3b) and the positions (cm^{-1}) of the absorption maxima in the experimental vibrational spectra of $MgZrF_6 \cdot 5H_2O$. For comparison, in Table 2, the IR and Raman frequencies are also presented for polycrystalline β-$BaZrF_6$ [21], which has a similar structure of the complex anion. According to calculations, the spectral range of 600–480 cm^{-1} mainly contains the stretching vibrations of the Zr–F_t bonds, while the Zr–F_b stretches fall with the range of 450–390 cm^{-1}. The contour of the bands from 600 to 400 cm^{-1} is considerably complicated since this frequency range covers δ_{lib}, δ_{wag}, and δ_{rock} modes related to the presence of water molecules and the hydrogen bonds they form in the structure.

The only lines that were not assigned in the experimental spectra are those probably related to the presence of Mg^{2+} ions, H_2O molecules and their interaction with the fluorozirconate lattice: 740, 592, 356, and 255 cm^{-1} (IR); 362 cm^{-1} (Raman). Table 3 lists the vibration frequencies for $Mg(H_2O)_{n \le 6}$, MgF_2, and $(MgF_2)_n$ [22–28], which can be compared with the spectrum of the studied compound. The bands at 740 and 592 cm^{-1} can be assigned to $\nu_{wag,rock,lib}$ vibrations of H_2O molecules. While the mode at 362 cm^{-1} can be assigned to both the $\nu_s(ZrF_b)$ (A_1) vibration of the fluorozirconate chain and to the $\nu_s(MgO_n)$ and $\nu_s(MgF_2)$ vibrations (Table 3), the intense IR band at 356 cm^{-1} can be attributed, as for $MgZrF_6$, only to the $\nu_{as}(MgF_2)$ vibration, in view of the fact that the Mg–F_t distances in the lattice are ~2.00 Å; i.e., rather strong bond

Table 2. Experimental IR and Raman spectra of $MgZrF_6 \cdot 5H_2O$ and calculated vibration frequencies, intensities, and band assignment for the $[Zr_4F_{26}]^{10-}$ anion (D_{2h})

Experiment $MgZrF_6 \cdot 5H_2O$		Assignment	Symmetry	β-$BaZrF_6$ [21]		DFT/321G		
IR ν, cm^{-1}	Raman ν, cm^{-1}			IR ν, cm^{-1}	Raman ν, cm^{-1}	$[Zr_4F_{26}]^{10-}$ (D_{2h})		
						N, cm^{-1}	IR, int.*	Raman, int.
740			–	–	–	–	–	–
592			–	–	–	–	–	–
	564	$\nu_s(ZrF_{4\,t})$	A_1		562	562	0.0	276.0
509		$\nu_{as}(ZrF_{4\,t})$	E	500–470		554 532	10.3 11.1	0.0 0.0
	485	$\nu_s(ZrF_{4\,t})$	B_2		480–470	496 481	0.0 2.7	119.0 0.0
455		$\nu_s(F_{2\,b})$ $\nu_{as}(F_{2\,b})$	A_1 B_2			429 410	0.0 0.1	74.0 0.2
395		$\nu_{as}(ZrF_{2\,b} - F_{2\,b})$	B_2		390	385	8.03	0.0
	362	sym comb ($\nu_s(ZrF_{4\,b})$) as comb ($\nu_s(ZrF_{4\,b})$)	A_1		380–350	390 366	0.0 0.0	175.0 0.0
356			–	–	–	–	–	–
323		$\delta_{\perp sciss}(ZrF_{2\,b} + ZrF_{2\,t})$	E			323	0.03	0.0
		$\delta_{\parallel sciss}(ZrF_{2\,b} + ZrF_{2\,t})$	E			293	0.3	0.0
		$\delta_{sciss}(ZrF_{4\,t}$ + rot $ZrF_{4\,b})$	B_2			280	0.0	2.0
275	289	$\gamma(ZrF_{4\,t})$	B_2	280–260	285	276 227	0.0 5.8	387.0 0.1
255			–	–	–	–	–	–
210		$\gamma(ZrF_{2\,t} - ZrF_{2\,t})$	A_1			224 205	0.0 0.8	357.0 0.0
		rot$(ZrF_{4\,b})$	A_2			197	0.0	0.4
	185	$\gamma(ZrF_{2\,t} + ZrF_{2\,b})$	E		188	187 180	0.0 0.1	0.4 0.0
	146	$\gamma(ZrF_{2\,t} - ZrF_{2\,b})$	E			147	0.0	18.0
		$\delta_{sciss}(ZrF_{4\,t}$ – rot $ZrF_{4\,b})$	B_1			210	0.0	0.1
Lattice		sym comb ($ZrF_n + ZrF_n$) as comb ($ZrF_n - ZrF_n$)	A_1 B_1			204 154	0.0 0.0	944.0 345.0

* The intensity of the calculated IR bands is expressed in $D^2/\mu A^2$, that of the Raman bands is in A^4/μ.

between Mg^+ and the fluorozirconate lattice is formed.

The IR spectrum of pentahydrate, apart from the ν_{as}(Mg–F) stretching band (350–370 cm^{-1}), also contains an additional band with the maximum at 255 cm^{-1}, probably, corresponding to the $\delta(MgF_2)$ bending vibrations of the $Mg(H_2O)_4F_2$ group (Table 3).

The broad intense H_2O stretching band at 3547–3261 cm^{-1} recorded in the IR spectrum of the pentahydrate (Fig. 3d) changes the shape and intensity on heating. The presence of several absorption maxima in this range shifted to lower frequency implies that hydrogen bonds that differ in energy are present in the structure [29]. The stronger $HOH\cdots OH_2$ hydrogen bond gives rise to lower OH vibration frequency (3358–3262 cm^{-1}), whereas the bands at 3547–3505 cm^{-1} refer to weaker HOH···FZr– hydrogen bonds. The region of 1700–1500 cm^{-1} exhibits two bending modes $\delta(H_2O)$

Table 3. Vibration frequencies and band assignment in the spectra of $[Mg(H_2O)_{n \leq 6}]^{2+}$, MgF_2, and $(MgF_2)_n$ from published data [22–28]

Published data		Symmetry	Assignment	Objects
ν, cm^{-1}				
IR	Raman			
770–720 [22]		T_u, T_g	$\nu_{wag, rock}(H_2O)$	$[Mg(H_2O)_6]^{2+} + (H_2O)_{12}$
620–540 [22]		T_u, T_g	$\nu_{wag, lib}(H_2O)$	
470–420 [22]		T_u	$\nu_{as}(MgO_n)$	$[Mg(H_2O)_6]^{2+}$
450–410 [27, 28]		E_u	$\nu_{as}(MgF_6)$	Solid MgF_2 $KMgF_3$
487–450 [26]		B_{2u}, B_{3u}	$\nu_{as}(MgF_2)$	Mg_2F_4
399 [27, 28]		A_{2u}	$\nu_{as}(MgF_2)$	Solid MgF_2 Solid $KMgF_3$
	420 [25]	A_1	$\nu_s(MgF_{2\ b})$	$(MgF_2)_2$ (D_{2h})
	405 [28]	A_{1g}	$\nu_s(MgF_6)$	Solid MgF_2
	380–350 [22]	A_{1g}	$\nu_s(MgO_6)$	$[Mg(H_2O)_6]^{2+}$
	360–320 [23]	A_g	$\nu_s(MgO_{n<6})$	$[Mg(H_2O)_{n<6}]^{2+}$
	353 [26]	A_g	$\nu_s(MgF_{2\ b})$	Mg_2F_4
	339 [25]		$\nu_s(MgF_{2\ b})$	$(MgF_2)_2$ (D_{2h})
337 [26]		B_2	$\nu_{as}(MgF_{2\ b})$	Mg_2F_4 (D_{2h})
330–310 [22, 24]		T_{1u}	$\nu_{as}(MgO_n + H_2O_{lib})$	$[Mg(H_2O)_6]^{2+} + (H_2O)_{12}$ $MgSO_4 \cdot 7H_2O$
310 [25]		E	$\nu_{as}(MgF_{2\ b})$	$(MgF_2)_2$ (D_{2h})
	315–250 [22]	E_g	$\nu_s(MgO_n)$	$[Mg(H_2O)_6]^{2+}$
	294 [28]	E_{1g}	$\nu_s(MgF_6)$	Solid MgF_2
	263–240 [22]	T	$\delta(MgO_6 + H_2O_{lib})$	$[Mg(H_2O)_6]^{2+} + (H_2O)_{12}$
	250–240 [22]	T_g	$\delta(MgO_6)$	$[Mg(H_2O)_6]^{2+}$
247 [28]		E_u	$\delta(MgF_6)$	Solid MgF_2
240 [26]		B_{1u}	$\delta(MgF_2)$	Mg_2F_4

(Fig. 3d), which supports the presence of coordinated and crystal H_2O molecules (1668 and 1637 cm^{-1}, respectively). The δ_{lib} and δ_{wag} vibrations of the coordinated water molecules bonded to magnesium occur at 740–750 cm^{-1}.

Vibrational spectra of $MgZrF_6 \cdot 2H_2O$. The intense broad absorption bands with pronounced maximum at 509 cm^{-1} (Fig. 3c, dashed line) are due to the Zr–F_t stretches. The complication of the ν_{as}(Zr–F) stretching band contour in the IR spectra of di- and pentahydrates and the shift of the band maximum to lower frequency compared with the IR spectrum of $MgZrF_6$ are the consequences of the increase in the Zr coordination number from 6 to 8 and the decrease in the symmetry of the ZrF_8^{4-} polyhedra in the crystal hydrate structure on passing from $MgZrF_6$ to $MgZrF_6 \cdot nH_2O$. The separation of the second component (419 cm^{-1}) in the IR spectrum of magnesium hexafluorozirconate dihydrate may be due to strengthening of the bridging bonds in the lattice following the decrease in the number of water molecules or the decrease in the number of hydrogen bonds with the bridging F_b atoms. As compared with the higher crystal hydrate, the IR spectrum of the dihydrate no longer exhibits the band at 455 cm^{-1}, possibly due to the decrease in the number of magnesium-coordinated H_2O molecules (Table 3); simultaneously, the $\nu_{as}(MgO_n)$ mode located in the $\nu_s(F_{b2})$ and $\nu_{as}(F_{b2})$ vibration region (455 cm^{-1}) shifts to higher frequency. The positions of the bending modes also change: whereas in the IR spectrum of the higher crystal hydrate, the intensity of 255, 275 cm^{-1} bands is substantially higher, in the spectrum of the low-water hydrate, the bands are shifted to higher frequency and are less intense. This also confirms the decrease in the degree of Mg coordination by H_2O molecules.

In the structures of compounds in question, the fraction of the Mg–F bonds increases in the series higher crystal hydrate–anhydrous compound, which is reflected in the increased intensity of the relevant bands ν_{as}(Mg–F) (356, 360, 369 cm^{-1}) in the IR spectra.

In the IR spectrum of $MgZrF_6 \cdot 2H_2O$, two H_2O absorption bands are observed in the stretching vibration range (3584, 3626 cm^{-1}) and one intense band in the bending vibration range $\delta(H_2O)$ (1635 cm^{-1}) (Fig. 3d). Presumably, both water molecules in the structure are equivalent and involved in symmetrical one-type H-bonds with the ZrF_8^{4-}, anion, and the observed doubling of the absorption bands in the stretching region can be attributed to the presence of H-bonds of water molecules with fluorine atoms having different length.

Thus, it was established that the transition from the magnesium hexafluorozirconate pentahydrate to anhydrous $MgZrF_6$ observed at temperatures of 50–420°C involves the formation of intermediate $MgZrF_6 \cdot 2H_2O$ phase stable below 150°C. Above 420°C, $MgZrF_6$ undergoes high-temperature hydrolysis that occurs according to the acid type and involves the cation.

Analysis of the IR and Raman spectra provides information about the structural features of the compounds. According to IR and Raman spectral data, the principal vibration bands of the functional groups are comparable for $MgZrF_6 \cdot 5H_2O$ and $MgZrF_6 \cdot 2H_2O$ and differ from those for $MgZrF_6$. This is indicative of the similar features (common structural units) in the lattices of the crystal hydrates and a change in the spatial configuration and Zr coordination number on going to the anhydrous compound.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 08-03-00355).

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