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Synthesis and Study of Hybrid Organic–Inorganic Glycinium Fluorozirconates

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Abstract—Hybrid organic–inorganic zirconium fluoride complexes, (GlyH)ZrF_5, (GlyH)$ZrF_5 \cdot 2H_2O$, and $(GlyH)_2ZrF_6$, have been synthesized for the first time. They were studied by X-ray powder diffraction and thermal analysis, as well as IR and Raman spectroscopy. The structure of the fluorozirconates was inferred from IR and Raman spectroscopic data.

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Hybrid organic–inorganic coordination compounds of metals have been intensively studied for the last decade owing to their valuable physical properties of these compounds and their potential for use. The data on hybrid organic–inorganic zirconium fluoride complexes are not numerous. Previously, we synthesized and structurally studied a large group of hybrid zirconium fluoride complexes with protonated alkyl amines as an organic component (tetramethylammonium [1], diethylammonium [2], ethylenediammonium [3–5], tetramethylenediammonium [6], hexamethylenediammonium [7], diethylenetriammonium [8–10], triethylenetetraammonium [11]), as well as guanidinium [12–14] and its derivatives (aminoguanidinium(+1) [15–16] and aminoguanidinium(+2) [16–18]). The synthesis, crystal structure, and thermal behavior of zirconium fluoride complexes $(C_2H_{10}N_2)Zr_2F_{10} \cdot H_2O$ and $(C_4H_{12}N_2)ZrF_6$, are also described in [19].

We have synthesized and structurally studied aminoguanidinium(+2) hexafluorozirconate, $CH_8N_4ZrF_6$ [16], which is considered as a new ferroelectric in [20]. It is known that many compounds with a glycinium cation undergo ferroelectric phase transitions. To search for new ferroelectrics among complex zirconium fluorides, we have synthesized for the first time hybrid organic–inorganic fluorozirconates with a glycinium cation as an organic component. This work is concerned with the synthesis of glycinium fluorozirconates, the determination of their composition, and their study by X-ray powder diffraction, thermal analyses, and IR and Raman spectroscopy.

EXPERIMENTAL

To synthesize glycinium fluorozirconates, an HF solution of zirconium fluoride with a known zirconium concentration and chemically pure glycine (Gly) were used as starting compounds. Zirconium fluoride solution was prepared by ZrO_2 dissolution in ~40% hydrofluoric acid under heating.

The interaction of glycine with a zirconium fluoride solution was studied in molar ratios of 0.25–(3 : 1). The products were studied by elemental analysis, thermal analysis, X-ray powder diffraction, and IR spectroscopy.

Glycinium fluorozirconates was synthesized using two procedures. Following the first procedure, calculated glycine amounts (corresponding to the molar ratio of the components) were added in small portions to the starting zirconium fluoride solution, which contained 2 g (0.022 mol) zirconium. In this case, glycine samples dissolved almost immediately. Then, the solutions were concentrated on a water bath until the beginning of crystal formation and allowed to stand for crystallization. The second procedure was the following. The solution was concentrated to half its starting volume after glycine addition. Then, the solution was allowed to stand for isothermally concentrating and slowly crystallizing at room temperature.

The precipitates obtained in the course of crystallization were separated from the mother solution by filtering on a Buckner funnel under vacuum, then they were washed with a small amount of acetone and dried in air for 8–10 h.

The products were analyzed for zirconium, fluorine, and H_2. X-ray powder diffraction patterns were recorded on a DRON 2.0 diffractometer (CuK_α radiation). The single-crystal X-ray diffraction experiments was carried out on a Bruker SMART 1000 CCD diffractometer. IR spectra were recorded on a Shimadzu IR Prestige 21 spectrophotometer and Raman spectra on a Bruker RFS 100/S spectrometer. The elemental, thermal, and X-ray diffraction analyses and spectroscopical studies ware carried out using standard procedures.

Table 1. Elemental analytical data and crystallographic parameters of glycinium fluorozirconates

Composition	Percentage, %			Crystal system, space group	Unit cell parameters				Z
	Zr	F	H_2O		a, Å	b, Å	c, Å	Angle, deg	
$(GlyH)ZrF_5 \cdot 2H_2O$*	30.37**/30.58	31.29/31.83	12.26/12.08	Monoclinic, $P2_1/c$	12.633(2)	6.636(2)	10.276(2)	β = 92.01(1)	4
$(GlyH)ZrF_5$	34.76/34.79	36.56/36.20							
$(GlyH)_2ZrF_6$	25.27/25.53	31.58/31.90		Triclinic, $P\bar{1}$	7.215(2)	9.108(2)	9.322(1)	α = 73.32(1) β = 74.32(1) γ = 70.62(1)	2

Notes: * GlyH is glycinium cation.

** Found (above the line), calcd. (below the line).

RESULT AND DISCUSSION

The studies of glycine reaction with zirconium fluoride solution showed that at the batch ratio (0.25–3) : 1 (mol/mol), three individual complex fluorides are formed. The chemical composition of these complexes depends both on the batch ratio and the conditions of crystallization from solution. For batch ratios of (0.25–3) : 1 – 1 : 1, rapid crystallization (concentrating until the beginning of crystallization) produces a fine crystalline precipitate of $(GlyH)ZrF_5$ (GlyH is a glycinium cation). At the same molar ratios of the starting compounds in the solution, slow crystallization at room temperature produces glycinium pentafluorozirconate dihydrate, $(GlyH)ZrF_5 \cdot 2H_2O$, in the form of well-shaped small crystals. The concentration of the (Gly : ZrO_2(HF) = 2 : 1) solution to a minimum volume increases its viscosity, but the crystallization of the product is not observed. However, careful stirring of this viscous solution for several minutes leads to the formation of a crystalline precipitate, which then was recrystallized from water (the solution pH 3). Well-formed small crystals of $(GlyH)_2ZrF_6$ are obtained as a result of crystallization from this solution. When the molar ratio of starting components is 3 : 1, the compound does not crystallize from the viscous solution (after concentration) even upon its long stirring.

The results of the elemental analysis of the synthesized hybrid glycinium fluorozirconates are displayed in Table 1. The compounds are colorless crystalline substances; they are well soluble in water, except for $(GlyH)ZrF_5$. Fluorozirconates $(GlyH)ZrF_5 \cdot 2H_2O$ and $(GlyH)_2ZrF_6$ can be recrystallized from water solution without the change in their composition. The solubility of anhydrous glycinium pentafluorozirconate in water is rather low.

The synthesized glycinium fluorozirconates are stable in air under standard ambient conditions. Complex $(GlyH)ZrF_5$ is thermally stable upon heating to 220°C. Starting at 230°C, it decomposes with the formation of ZrO_2 as a final product. The thermoanalytical data shows that the dehydration of $(GlyH)ZrF_5 \cdot 2H_2O$ at a heating rate of 10 K/min proceeds in the temperature interval 50–100°C in one stage and is accompanied by the formation of $(GlyH)ZrF_5$, which, according to the X-ray powder diffraction and IR spectroscopic data, is identical to the anhydrous glycinium pentafluorozirconate isolated from solution.

The X-ray diffraction parameters were determined for the synthesized fluorozirconates $(GlyH)ZrF_5 \cdot 2H_2O$ and $(GlyH)_2ZrF_6$ crystallized from solution in the form of single crystals (Table 1). The crystals $(GlyH)ZrF_5 \cdot 2H_2O$ are monoclinic, space group $P2_1/c$, $Z = 4$. The crystals of $(GlyH)_2ZrF_6$ are triclinic, space group $P1$, $Z = 2$.

The X-ray powder diffraction patterns of $(GlyH)ZrF_5 \cdot 2H_2O$ and $(GlyH)_2ZrF_6$ with the unit cell parameters determined from single-crystal data were calculated by the procedure in [21]. The results are displayed in Table 2. Single crystals of $(GlyH)ZrF_5$ were not obtained; Table 3 displays interplanar spacings and diffraction intensity, which can be used for the identification of this complex.

Provisional data on the structure of glycinium fluorozirconates were obtained using vibration spectroscopy. The vibration frequencies found in the IR and Raman spectra of the studied glycinium fluorozirconates and their assignment are given in Table 4.

The organic component of the synthesized hybrid zirconium fluoride complexes is a glycinium cation, whose IR and Raman spectra are described in detail [22, 23].

In the IR and Raman spectra of the synthesized hybrid zirconium fluoride complexes (Table 4) in the region 3300–700 cm^{-1}, there are many absorption bands corresponding to the vibrations of N–H, C–H, C–N, and C=O (C–O) bonds of the glycinium cation. The absorption bands of Zr–F bonds in the vibration

Table 2. X-ray powder diffraction data for glycinium fluorozirconates

I, %	*d*, Å		*hkl*	*I*, %	*d*, Å		*hkl*
	exp.	calcd.			exp.	calcd.	
$(GlyH)ZrF_5 \cdot 2H_2O$							
100	12.81	12.63	100	9	1.957	1.957	330
80	6.30	6.31	200	8	1.926	1.926	232
7	5.56	5.57	011	9	1.912	1.914	513
37	5.13	5.13	$\bar{1}11$	5	1.886	1.888	$\bar{5}22$
23	5.07	5.07	111	8	1.854	1.854	522
18	4.80	4.82	$\bar{1}02$	7	1.841	1.843	$\bar{1}33$
17	4.70	4.70	102	7	1.831	1.831	$\bar{5}04$
3	4.56	4.57	210	8	1.801	1.801	$\bar{3}15$
49	4.21	4.22	$\bar{2}11$	7	1.791	1.791	$\bar{2}33$
25	4.13	4.14	211	5	1.770	1.770	504
16	4.05	4.05	$\bar{2}02$	4	1.755	1.755	$\bar{6}13$
14	3.92	3.92	202	3	1.719	1.719	$\bar{7}02$
9	3.83	3.84	112	6	1.704	1.704	$\bar{1}06$
3	3.45	3.46	$\bar{2}12$	19	1.682	1.683	702
3	3.38	3.37	212	3	1.666	1.666	$\bar{1}34$
25	3.31	3.31	$\bar{3}02$	4	1.658	1.658	016
20	3.20	3.20	302	3	1.643	1.643	415
10	3.15	3.15	400	2	1.612	1.611	234
12	3.04	3.04	013	3	1.603	1.603	$\bar{5}24$
12	2.98	2.98	$\bar{1}13$	3	1.584	1.584	720
28	2.93	2.94	220	5	1.576	1.577	042
2	2.81	2.81	221	3	1.567	1.567	$\bar{3}34$
14	2.78	2.78	$\bar{2}13$	5	1.525	1.525	316
7	2.73	2.73	$\bar{4}02$	11	1.510	1.509	425
5	2.65	2.65	402	3	1.499	1.499	$\bar{7}04$
3	2.56	2.57	$\bar{2}22$	4	1.482	1.482	342
30	2.52	2.52	500	1	1.466	1.466	434
3	2.50	2.50	$\bar{3}13$	2	1.444	1.444	$\bar{3}26$
11	2.431	2.431	313	2	1.440	1.439	$\bar{2}07$
1	2.377	2.382	023	2	1.427	1.428	335
3	2.344	2.343	$\bar{3}22$	2	1.419	1.419	714
2	2.315	2.315	$\bar{5}11$	3	1.404	1.404	442
14	2.222	2.224	$\bar{4}13$	3	1.385	1.385	540
11	2.156	2.158	413	4	1.378	1.378	$\bar{7}05$
11	2.125	2.129	131	2	1.353	1.354	426
13	2.101	2.102	600	2	1.306	1.306	606
3	2.038	2.038	$\bar{1}05$	3	1.302	1.301	640
3	2.026	2.026	$\bar{4}04$	2	1.268	1.268	$\bar{6}42$
5	2.006	2.004	610	1	1.249	1.249	$\bar{8}\,15$
11	1.973	1.973	$\bar{2}05$				

Table 2. (Contd.)

I, %	*d*, Å		*hkl*	*I*, %	*d*, Å		*hkl*
	exp.	calcd.			exp.	calcd.	
			$(GlyH)_2ZrF_6$				
20	8.42	8.41	010	4	2.65	2.65	$2\bar{1}\bar{1}$
8	6.84	6.86	011	14	2.62	2.62	$22\bar{1}$
34	6.73	6.76	100	4	2.59	2.59	223
100	6.11	6.12	110	3	2.51	2.51	$03\bar{1}$
56	5.93	5.91	101	8	2.494	2.495	$2\bar{1}2$
58	5.49	5.48	$01\bar{1}$	4	2.459	2.457	$1\bar{1}\bar{3}$
10	4.89	4.88	$10\bar{1}$	3	2.393	2.391	$21\bar{2}$
21	4.36	4.36	$11\bar{1}$	7	2.347	2.346	233
5	4.28	4.29	012	7	2.304	2.299	$2\bar{1}\bar{2}$
15	4.21	4.20	020	7	2.246	2.245	320
33	4.16	4.16	021	10	2.231	2.233	142
59	4.10	4.10	120	7	2.179	2.180	$02\bar{3}$
10	4.05	4.04	102	9	2.156	2.156	331
65	3.67	3.66	122	6	2.115	2.113	$31\bar{1}$
42	3.60	3.60	211	8	2.080	2.081	134
6	3.56	3.57	$01\bar{2}$	6	2.040	2.041	330
6	3.50	3.50	$02\bar{1}$	3	2.014	2.014	$20\bar{3}$
12	3.44	3.43	022	3	1.921	1.923	$3\bar{1}\bar{1}$
16	3.38	3.38	$10\bar{2}$	7	1.907	1.908	$2\bar{3}0$
10	3.30	3.31	$12\bar{1}$	18	1.892	1.892	324
3	3.26	3.25	221	4	1.859	1.860	$31\bar{2}$
4	3.21	3.21	$1\bar{1}2$	6	1.818	1.818	$2\bar{1}4$
3	3.17	3.17	$1\bar{1}\bar{2}$	4	1.792	1.792	411
15	3.09	3.09	$11\bar{2}$	4	1.780	1.780	251
13	3.06	3.06	220	4	1.743	1.743	$1\bar{2}4$
3	3.03	3.03	131	4	1.731	1.731	253
16	2.97	2.97	013	4	1.722	1.722	051
23	2.87	2.87	123	7	1.701	1.701	250
6	2.81	2.81	030	18	1.651	1.652	430

spectra of fluorozirconates are in the long-wave region (600–300 cm^{-1}), therefore they can be easily identified in the obtained compounds.

In the IR spectrum of $(GlyH)ZrF_5 \cdot 2H_2O$, a broad, middle intensity absorption band with weakly resolved peaks at 1946 and 1958 cm^{-1} is present along with the bands of glycinium cation and the bands of the stretching (3520 and 3435 cm^{-1}) and bending (1694 and 1653 cm^{-1}) vibrations of crystal water molecules. This band is absent in the Raman spectrum of $(GlyH)ZrF_5 \cdot 2H_2O$, as well as in the IR and Raman spectra of $(GlyH)_2ZrF_6$ and $(GlyH)ZrF_5$ obtained either from solution or upon dehydration of $(GlyH)ZrF_5 \cdot 2H_2O$. The presence of this band in the IR spectrum of $(GlyH)ZrF_5 \cdot 2H_2O$ may be explained by the formation of rather strong hydrogen bonds O–H···O between the OH of the carboxyl and the oxygen atom of the water molecule. It is possible that this compound can manifest phase transitions and valuable physical properties owing to the presence of strong H bonds.

Unlike the IR spectra of $(GlyH)ZrF_5 \cdot 2H_2O$ and $(GlyH)ZrF_5$, where the stretching vibrations of the NH_3^+ group appear as two intense, rather narrow, and well-resolved absorption bands at 3280 and 3100 cm^{-1},

Table 3. Interplanar spacings and diffraction intensities for (GlyH)ZrF_5

I, %	d, Å	I, %	d, Å	I, %	d, Å
100	10.05	2	2.73	3	1.743
2	7.63	1	2.71	3	1.708
5	5.54	2	2.68	3	1.698
10	5.41	2	2.63	3	1.677
75	4.97	2	2.60	2	1.665
4	4.42	3	2.52	5	1.656
8	4.29	18	2.487	1	1.638
3	4.17	4	2.449	1	1.614
26	3.75	3	2.401	3	1.565
25	3.65	3	2.374	2	1.551
20	3.56	1	2.315	1	1.537
13	3.49	1	2.282	1	1.525
7	3.43	2	2.217	2	1.508
6	3.37	4	2.151	2	1.478
20	3.32	2	2.096	2	1.429
3	3.25	4	2.069	2	1.420
3	3.22	11	1.987	1	1.406
6	3.16	10	1.933	2	1.392
3	3.11	7	1.916	2	1.380
3	3.08	8	1.885	2	1.362
3	2.98	9	1.866	1	1.328
1	2.92	10	1.838	2	1.301
3	2.87	7	1.804		
10	2.82	4	1.782		

in the IR spectrum of $(GlyH)_2ZrF_6$ these absorption bands merge and shift to the long-wave region (the maximum of this broad line is at 3103 cm^{-1}), which points to the formation of stronger hydrogen bonds N–H···F in the structure of this complex.

The inorganic part of the synthesized hybrid fluorozirconates consist of fluoride complex anions $[ZrF_5]^-$ and $[ZrF_6]^{2-}$, as well as crystal water molecules. The vibrational spectra of zirconium fluoride complexes and compounds including crystal water molecules are well studied [24].

The $(GlyH)_2ZrF_6$ compound includes complex anions $[ZrF_6]^{2-}$. In the structurally studied hexafluorozirconates, the complex anions $[ZrF_6]^{2-}$ can have both mononuclear (octahedral), binuclear, tetranuclear, or polynuclear chain structure.

The IR spectra of compounds with insular octahedral complex anions $[ZrF_6]^{2-}$ contain one intense absorption band in the region 480–515 cm^{-1} due to the stretching vibrations of the Zr–F bonds. In the IR spectra of hexafluorozirconates with binuclear and polynuclear complex anions, the frequencies of the stretching vibrations of the terminal Zr–F bonds are in the region 400–600 cm^{-1}, whereas the absorption band in the region 300–400 cm^{-1} corresponds to the bridging Zr–F–Zr bonds.

The stretching vibrations of the terminal Zr–F bonds in the IR spectrum of $(GlyH)_2ZrF_6$ (Table 4) appear as an intense broadened absorption band with a maximum at 480 cm^{-1} and a shoulder at 471 cm^{-1}, as well as two quite narrow middle-intensity absorption bands at 552 and 419 cm^{-1}. The IR spectrum of $(GlyH)_2ZrF_6$ also contains a middle-intensity band at 361 cm^{-1}, which may be assigned to the vibrations of the bridging Zr–F–Zr bonds. In the Raman spectrum of $(GlyH)_2ZrF_6$ the bridging Zr–F–Zr bonds appear as a broad weak band with two peaks at 394 and 378 cm^{-1}.

In the region of the stretching vibrations of Zr–F bonds, the IR spectrum of $(GlyH)_2ZrF_6$ is similar to the IR spectrum of the $(C_2H_{10}N_2)ZrF_6$ [3]; the latter is built of $C_2H_{10}N_2^{2+}$ cations and binuclear complex anions $[Zr_2F_{12}]^{4-}$ consisting of two pentagonal bipyramids ZrF_7 bound by a common F–F edge in the equatorial plane [4]. Therefore, one may conclude that the complex anions $[ZrF_6]^{2-}$ in $(GlyH)_2ZrF_6$ are also binuclear. In this case, the coordination number of the Zr atom is seven. The X-ray diffraction study of $(GlyH)_2ZrF_6$ crystals confirmed this assumption.

In the region 400–600 cm^{-1} of the IR spectrum of(GlyH)$ZrF_5 \cdot 2H_2O$, there are four absorption bands: two intense bands at 598 and 457 cm^{-1} and two low-intensity bands with peaks at 561 and 511 cm^{-1}. The significant short-wave shift of the frequency of the Zr–F stretches (598 cm^{-1}) in the IR spectrum of (GlyH)$ZrF_5 \cdot 2H_2O$ compared to the maximum frequency of the Zr–F stretches (552 cm^{-1}) in the IR spectrum of $(GlyH)_2ZrF_6$ is due to the greater proportion of the bridging F atoms in the structure of (GlyH)$ZrF_5 \cdot 2H_2O$ compared to the structure of $(GlyH)_2ZrF_6$. This fact is also confirmed by a significant increase of the intensity of the band of the stretching vibration of

Table 4. Vibration frequencies and their assignment in the IR and Raman spectra of glycinium fluorozirconates

$(GlyH)_2ZrF_6$		$(GlyH)ZrF_5 \cdot 2H_2O$		$(GlyH)ZrF_5$		Assignment
IR	Raman	IR	Raman	IR	Raman	
		3520 s				$\nu(H_2O)$
		3435 s				
3160 sh 3103 vs br		3265 vs	3268 w	3279 vs	3281 w	$\nu(NH_3^+)$
	3098 w	3103 m	3099 w	3130 vs br	3133 w	
3063 s br	3039 m	3034 w	3025 m	3043 w	3043 m	$\nu_{as}(CH_2)$
	2981 s		2985 s		2996 s	$\nu_s(CH_2)$
2700 w		2772 w		2718 w		
2567 w		2652 w		2610 w		
2448 w		2442 w		2519 w		
2372 w		2359 w		2376 w		
		1958 m br 1946				
1753 vs	1760 s	1746 m	1772 m	1745 vs	1743 vs	$\nu(C{=}O)$
		1694 m				$\delta(H_2O)$
		1653 m				
1614 m	1623 m	1624 m	1622 m	1614 m	1615 m	$\delta(NH_3^+)$
1595 m	1597 m	1609 m	1601 m	1587 m	1586 m	
1514 s	1510 w	1518 m	1525 w	1504 s	1509 w	
1425 m	1424 m	1435 w	1434 m	1445 vs	1444 vs	$\delta(CH_2)$
1310 w	1309 m	1317 s	1323 m	1330 w	1313 m	$\tau(CH_2)$
1236 vs	1227 m	1260 m	1252 w	1204 s	1202 m	$\nu(C–O)$
1136 m		1141 w	1133 m			
1119 m	1113 m	1126 m		1103 m	1107 m	$\rho(NH_3^+)$
1042 m	1045 m	1040 m	1035 m	1051 m	1052 s	$\nu(CN)$
922 s	927 w	924 m				
907 m				908 s	910 w	$\rho(CH_2)$
872 m	872 vs	874 m	884 vs	860 m	857 vs	$\nu(CC)$
821 w	750 m		666 w	797 s		
656 w	655 m	648 sh		648 m	648 m	$\delta(COOH)$
		598 s				$\nu(Zr–F)$
552 m	566 s 546 sh	561 w	563 vs	561 vs	578 m	
480 vs br 471 sh				502 s	543 vs	
	513 w br 492	511 w	507 s	467 vs 457 sh	499 s	
419 m		457 s	479 m		454 w	
361 m	394 w br 378	395 vs	386 m br 360	376 m	399 sh 384 m br	$\nu(Zr–F–Zr)$

bridging Zr–F–Zr bonds in the IR spectrum of (GlyH)$ZrF_5 \cdot 2H_2O$. This band is the most intense band of the stretching vibrations of the Zr–F bonds in the spectrum. A significant increase of the frequency of the stretching vibrations of the bridging Zr–F–Zr bonds (395 cm^{-1}) is observed compared to the analogous frequency (361 cm^{-1}) in the IR spectrum of $(GlyH)_2ZrF_6$ (Table 4). In the Raman spectrum of (GlyH)$ZrF_5 \cdot 2H_2O$, the stretching vibration of the bridging Zr–F–Zr bonds appear as a broad middle-intensity band with two peaks at 386 and 360 cm^{-1}. In this case, the band at 360 cm^{-1} is more intense than that at 386 cm^{-1}. The IR and Raman spectroscopic data allowed us to conclude that (GlyH)$ZrF_5 \cdot 2H_2O$ has a polynuclear structure, where there must be more bridging Zr–F–Zr bonds than terminal Zr–F bonds. According to the X-ray diffraction data, the complex anions in (GlyH)$ZrF_5 \cdot 2H_2O$ possess a polynuclear layered structure. In a polymeric layer, the zirconium polyhedra (ZrF_8) are bound through three common F–F edges. Thus, in each Zr polyhedron of the crystal structure of (GlyH)$ZrF_5 \cdot 2H_2O$, there are two terminal fluorine atoms for six bridging fluorine atoms.

In the region of the stretching frequencies of the Zr–F bonds (350–600 cm^{-1}), the IR spectra of (GlyH)$ZrF_5 \cdot 2H_2O$ and (GlyH)ZrF_5 (Table 4) are different in both the arrangement and the intensity of the absorption bands, which is due to the different structures of the complex anions.

In the IR spectrum of (GlyH)ZrF_5 in the region 400–600 cm^{-1}, there are two intense somewhat broadened absorption bands. A high-frequency band with a peak at 467 cm^{-1} and a bend at 457 cm^{-1} is overlapped by a narrow middle-intensity band with a peak at 502 cm^{-1}. The low-frequency band with a peak at 561 cm^{-1} is asymmetric and possesses an insignificant bend at ~570 cm^{-1}. The band of the stretching vibrations of the bridging Zr–F–Zr bonds in the IR spectrum of (GlyH)ZrF_5 is less intense than the corresponding band in the spectrum of (GlyH)$ZrF_5 \cdot 2H_2O$, but it is more intense than the analogous band in the IR spectrum of $(GlyH)_2ZrF_6$. The spectroscopic data allowed us to conclude that the structure of the synthesized anhydrous pentafluorozirconate is polynuclear. The degree of polymerization of this complex (the number of bridging F atoms in the polyhedron compared to the number of the terminal F atoms) must be lesser than in the structure of (GlyH)$ZrF_5 \cdot 2H_2O$ but greater than in the structure of $(GlyH)_2ZrF_6$.

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