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New Zirconium Fluoride Complexes $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs): Synthesis and Physicochemical Properties

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Abstract—Ammonium-containing zirconium fluoride complexes of the formula $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs) were obtained and studied. The complexes crystallize in the orthorhombic system. Their unit cell parameters were determined. The IR absorption spectra of the complexes in the 350–4000 cm^{-1} range were recorded and examined.

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Earlier, we have obtained ammonium-containing fluoride complexes of zirconium and hafnium of the formulas $(NH_4)_6MA_4F_{23}$ and $(NH_4)_6MA_3A'F_{23}$ (M = Li and Na; A and A' = Zr and Hf, respectively) [1] and determined the crystal structure of the complex $(NH_4)_6LiZr_4F_{23}$ [2]. Its structure is built from separate infinite anionic chains $[Zr_4F_{23}]^{7-}_{\infty}$ running parallel to each other along the axis x, with the interleaved cations NH_4^+ and Li^+. The zirconium polyhedra with the coordination numbers 7 and 8 share the edges F(2)···F(2)' or F(1)···F(1)'. The chains show distinguishable tetranuclear fragments $–[ZrF_7–ZrF_8–ZrF_8–ZrF_7]–$. The zirconium polyhedra in these fragments share common edges; the tetramers are linked together by the bridging F(6) atoms. For many zirconium fluoride complexes, this type of linkage of coordination polyhedra has not yet been documented.

According to NMR data [2, 3], the complexes $(NH_4)_6LiZr_4F_{23}$ and $(NH_4)_6NaZr_4F_{23}$ show unusual translational diffusion in the proton and fluoride subsystems in a temperature range from 415 to 440 K. Phase transitions in $(NH_4)_6NaZr_4F_{23}$ occur at 360–370 and 410–415 K; in the crystals of $(NH_4)_6LiZr_4F_{23}$, they are observed at 415 K. Both complexes have high electric conductivity ($\sigma \approx 4 \times 10^{-3}$ S/cm at 420 K) and are classified among superionic conductors.

The unusual structure of $(NH_4)_6LiZr_4F_{23}$ as well as the high ionic conductivity of $(NH_4)_6Li(Na)Zr_4F_{23}$ prompted us to obtain and study in more detail new complexes of this class. Here we described the synthesis and some of the properties of the complexes $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs).

EXPERIMENTAL

Appropriate alkali metal fluorides (reagent grade), ammonium fluoride (reagent grade), zirconium oxide (special purity grade), and hydrofluoric acid (reagent grade) were used.

Synthesis of zirconium fluoride complexes. Zirconium oxide was dissolved with heating on a water bath in 40% HF until a transparent solution formed. Then K(Rb, Cs)F and NH_4F were added simultaneously. The resulting mixture was stirred to complete homogenization and concentrated to initiate crystallization. The ratio of ZrO_2 : K(Rb, Cs)F : NH_4F was varied in the ranges (1–4) : (1–2) : (1–6).

The complexes obtained were identified by chemical analysis, X-ray powder diffraction, and IR spectroscopy.

Fluorine was determined as described in [4]; the alkali metals and zirconium were determined by atomic absorption spectroscopy on a Jarrel Ash AA-780 instrument. In addition, the zirconium content was determined by gravimetry for ZrO_2 obtained as follows. A weighed sample of the complex was treated with concentrated H_2SO_4, zirconium was precipitated with ammonia, and the precipitate was calcined at 800°C. The NH_4^+ content was determined using the Kjeldahl method [5].

X-ray powder diffraction patterns were recorded on a D8 ADVANCE diffractometer (CuK_α radiation). The unit cell parameters of the complexes obtained were determined by iteratively indexing the powder diffraction patterns using the single-crystal X-ray diffraction data for isostructural complexes. The specific densities of the complexes were measured by pycnometry in toluene at 25°C.

Table 1. Chemical analysis data for the ammonium-containing zirconium fluoride complexes

Complex	Content (found/calculated), %			
	NH_4	M	Zr	F
$(NH_4)_6KZr_4F_{23}$	11.2/11.4	4.3/4.1	38.1/38.4	45.8/46.1
$(NH_4)_6RbZr_4F_{23}$	10.6/10.9	8.2/8.6	36.5/36.6	44.0/43.9
$(NH_4)_6CsZr_4F_{23}$	10.3/10.4	12.3/12.7	35.5/35.0	42.0/41.9

Table 2. Unit cell parameters for the complexes $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs)*

Complex	Unit cell parameters, Å			Density, g/cm^3	
	a	*b*	*c*	found	calculated
$(NH_4)_6KZr_4F_{23}$	30.178(5)	25.150(3)	6.642(1)	2.48	2.50
$(NH_4)_6RbZr_4F_{23}$	30.149(5)	25.302(3)	6.650(1)	2.59	2.61
$(NH_4)_6CsZr_4F_{23}$	31.622(5)	26.113(3)	6.651(1)	2.50	2.53

* $Z = 8$.

IR absorption spectra (Nujol) were recorded on an IFS EQUINOX 55S spectrometer in the 350–4000 cm^{-1} range with an accuracy of 0.5 cm^{-1}.

RESULTS AND DISCUSSION

X-ray powder diffraction revealed that the complexation reactions for ZrO_2 : K(Rb, Cs)F : NH_4F = (1–2) : (1–2) : (1–3) give mixtures of ammonium and alkali metal hexafluoride and heptafluoride complexes. An unknown phase, apart from $(NH_4)_2ZrF_6$, was discovered for ZrO_2 : K(Rb, Cs)F : NH_4F = (3–4) : (1–2) : (4–5) and isolated in the individual state for ZrO_2 : K(Rb, Cs)F : NH_4F = 3 : 1 : 4. According to chemical analysis data, these phases can be formulated as $(NH_4)_4MZr_3F_{17} \cdot 2HF$ (M = K, Rb, and Cs). Lithium and sodium analogs have been synthesized earlier [6]. For ZrO_2 : K(Rb, Cs)F : NH_4F = 4 : 1 : 6, we obtained new complexes corresponding to the formula $(NH_4)_6MZr_4F_{23}$. Chemical analysis data for the latter complexes are given in Table 1.

The zirconium fluoride complexes obtained are colorless crystalline solids that are stable in air, are well soluble in water, and can be recrystallized from water without any changes in their compositions.

All these complexes crystallize in the orthorhombic system. Their unit cell parameters were determined using the parameters found from the single-crystal X-ray diffraction patterns of $(NH_4)_6NaZr_4F_{23}$ [1]. The crystallographic data[1] for the complexes obtained were used for their identification. The density of $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs) calculated for eight formula units per unit cell is in satisfactory agreement with pycnometric data. The similarity of the diffraction patterns for $(NH_4)_6KZr_4F_{23}$, $(NH_4)_6RbZr_4F_{23}$, and $(NH_4)_6CsZr_4F_{23}$ as well as their close unit cell parameters (Table 2) suggest that these complexes are isostructural.

Table 3. Absorption peaks (cm^{-1}) for the stretching vibrations of the ammonium groups and fluorozirconate polyhedra in the IR spectra of $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs)

Complex	ν(N–H)	ν(A–F)
$(NH_4)_2ZrF_6$	3226, 3080	565, 472
$(NH_4)_6KZr_4F_{23}$	3252, 3080	581, 487, 399
$(NH_4)_6RbZr_4F_{23}$	3247, 3087	541, 480, 445
$(NH_4)_6CsZr_4F_{23}$	3237, 3077	585, 491, 392, 378
$(NH_4)_6LiZr_4F_{23}$ [1]	3240, 3080	588, 525, 484, 398
$(NH_4)_6NaZr_4F_{23}$ [1]	3247, 3080	584, 485, 398

The IR spectra of the complexes obtained (figure) in the 600–400 cm^{-1} range show intense absorption bands of complicated shape. Comparison of these IR spectra with those of some crystalline fluorozirconates [7], including heterocationic ones [1, 8–10], allows assigning these bands to the Zr–F stretching vibrations in fluorozirconate groups. The complicated shapes of the bands assigned to the vibrations of the fluorozirconate polyhedron in the similar IR spectra of the complexes under discussion and $(NH_4)_6LiZr_4F_{23}$ (Table 3) can be explained by a number of reasons. The first reason is the presence of the polyhedra with different coordination numbers (7 and 8), as in $(NH_4)_6LiZr_4F_{23}$ [2]. The second reason is the presence of the bridging and nonbridging F atoms, or the bridges with different strengths, which is due to the different coordination numbers of the polyhedra as

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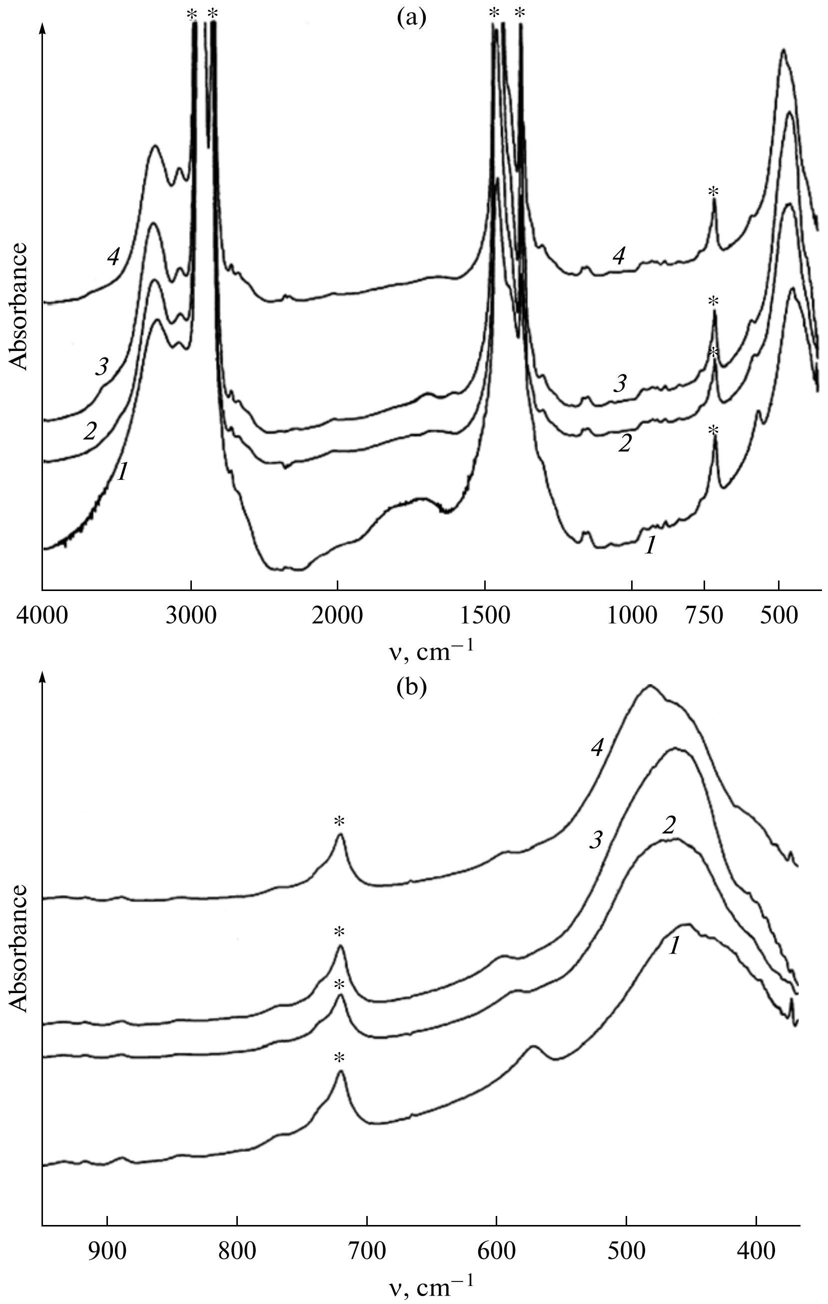
[1] The indexing results for the powder diffraction patterns of the zirconium fluoride complexes obtained can be made available from the authors upon request.



(a) The IR absorption spectra of the zirconium fluoride complexes: (*1*) $(NH_4)_2ZrF_6$, (*2*) $(NH_4)_6KZr_4F_{23}$, (*3*) $(NH_4)_6RbZr_4F_{23}$, and (*4*) $(NH_4)_6CsZr_4F_{23}$; (b) the fragments of the IR spectra in the 350–900 cm^{-1} range.

well as to the different ways of their linkage. This is evident from the fact that the band assigned to the fluorozirconate stretching vibrations in the IR spectra of the complexes under study is substantially broader than that in the IR spectrum of $(NH_4)_2ZrF_6$ (figure). It is known [11] that the structure of $(NH_4)_2ZrF_6$, in contrast to the complexes under consideration, is built from bridged polyhedra with C.N. 8. Finely, the complicated shape of the band in the 600–400 cm^{-1} range is partly due to the distortion of the polyhedra exposed to the cationic environment.

The presence of the ammonium groups in the complexes obtained is undoubted and confirmed by the presence of intense absorption bands at 3300–3000 and 1300–1400 cm^{-1} (figure). The positions of the bands corresponding to the N–H stretching vibrations in the ammonium groups (3300–3000 cm^{-1}) only slightly depend on the second outer-sphere cation; according to the frequencies of the ν_3(N–H) stretching vibrations, the hydrogen bonds are virtually as strong as those in the crystalline complexes $(NH_4)_2ZrF_6$ and $(NH_4)_6Na(Li)Zr_4F_{23}$ (Table 3).

To sum up, we developed the conditions for the synthesis of a wider range of zirconium fluoride complexes with heteroatomic cationic sublattices. The X-ray diffraction patterns and IR spectra of the ammonium-containing complexes $(NH_4)_6MZr_4F_{23}$ (M = K, Rb, and Cs) we obtained suggest their possible chain structures. If it is the case, these chain fluoride complexes, like $(NH_4)_6LiZr_4F_{23}$ [2, 3, 11, 12], can be regarded as potential compounds with high ionic conductance. This assumption will be verified in a further study of the dynamics of fluoride and ammonium ions, with measurement of the electric conductivity of the complexes obtained.

REFERENCES

1. Antokhina, T.F., Ignat'eva, L.N., Savchenko, N.N., and Kaidalova, T.A., *Russ. J. Inorg. Chem.*, 2004, vol. 49, no. 9, p. 1314.
2. Gerasimenko, A.V., Kavun, V.Ya., Sergienko, V.I., and Antokhina, T.F., *Russ. J. Coord. Chem.*, 1999, vol. 25, no. 8, p. 562.
3. Kavun, V.Ya., Sergienko, V.I., Uvarov, N.F., and Antokhina, T.F., *Zh. Strukt. Khim.*, 2002, vol. 43, no. 3, p. 464.
4. Willard, H.H. and Winter, O.B., *Ind. Eng. Chem. Anal. Ed.*, 1933, vol. 5, p. 7.
5. Petrashen', V.I., *Ob"emnyi analiz* (Volumetric Analysis), Moscow: Goskhimizdat, 1946.
6. Antokhina, T.F., Ignat'eva, L.N., Kaidalova, T.A., and Savchenko, N.N., *Russ. J. Coord. Chem.*, 2003, vol. 29, no. 3, p. 157.
7. Davidovich, R.L., Kaidalova, T.A., Levchishina, T.F., and Sergienko, V.I., *Atlas infrakrasnykh spektrov pogloshcheniya i rentgenometricheskikh dannykh kompleksnykh ftoridov metallov IV i V grupp* (Atlas of Infrared Absorption Spectra and X-Ray Diffraction Data for Complex Fluorides of Group IV and V Metals), Moscow: Nauka, 1972.
8. Antokhina, T.F., Ignat'eva, L.N., Kavun, V.Ya., et al., *Russ. J. Inorg. Chem.*, 2002, vol. 47, no. 9, p. 1271.
9. Antokhina, T.F., Ignat'eva, L.N., Savchenko, N.N., et al., *Russ. J. Inorg. Chem.*, 2003, vol. 48, no. 12, p. 1871.
10. Kavun, V.Ya., Sergienko, V.I., Chernyshov, B.N., et al., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 4, p. 1004.
11. Kavun, V.Ya., Gerasimenko, A.V., Sergienko, V.I., et al., *Zh. Prikl. Khim.*, 2000, vol. 73, no. 6, p. 966.
12. Kavun, V.Ya. and Sergienko, V.I., *Diffuzionnaya podvizhnost' i ionnyi transport v kristallicheskikh i amorfnykh ftoridakh elementov IV gruppy i sur'my(III)* (Diffusion Mobility and Ion Transport in Crystalline and Amorphous Fluorides of Group IV Elements and Antimony(III)), Vladivostok: Dal'nauka, 2004.