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Synthesis and crystal structures of zirconium(IV) nitrate complexes $(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$, $Cs[Zr(NO_3)_5]$, and $(NH_4)[Zr(NO_3)_5](HNO_3)$

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The zirconium nitrate complexes $(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$ (**1**), $Cs[Zr(NO_3)_5]$ (**2**), $(NH_4)[Zr(NO_3)_5](HNO_3)$ (**3**), and $(NO_2)_{0.23}(NO)_{0.77}[Zr(NO_3)_5]$ (**4**) were prepared by crystallization from nitric acid solutions in the presence of H_2SO_4 or P_2O_5. The complexes were characterized by X-ray diffraction. The crystal structure of **1** consists of nitrate anions, nitronium cations, and $[Zr(NO_3)_3(H_2O)_3]^+$ complex cations in which the Zr^{IV} atom is coordinated by three water molecules and three bidentate nitrate groups. The coordination polyhedron of the Zr^{IV} atom is a tricapped trigonal prism formed by nine oxygen atoms. The island structures of **2** and **3** contain $[Zr(NO_3)_5]^-$ anions and Cs^+ or $NH_4{}^+$ cations, respectively. In addition, complex **3** contains HNO_3 molecules. Complex **4** differs from $(NO_2)[Zr(NO_3)_5]$ in that three-fourth of the nitronium cations in **4** are replaced by nitrosonium cations NO^+, resulting in a decrease in the unit cell parameters. In the $[Zr(NO_3)_5]^-$ anion involved in complexes **2**—**4**, the Zr^{IV} atom is coordinated by five bidentate nitrate groups and has an unusually high coordination number of 10. The coordination polyhedron is a bicapped square antiprism.

Key words: zirconium(IV) nitrate complexes, crystal structure, X-ray diffraction analysis.

Until recently, only a few zirconium(IV) nitrate complexes were known, which is associated with the fact that these complexes are highly prone to hydrolysis giving rise to zirconyl derivatives. For example, zirconyl nitrate hydrate $ZrO(NO_3)_2 \cdot 2H_2O$ generally crystallizes from nitric acid solutions. The crystal structure of this compound consists of the infinite OH-bridged $[Zr(NO_3)_2(OH)_2]_n$ chains, which are linked to each other through crystallization water molecules.[1] Crystalline precipitates, which decomposed in air to form $ZrO(NO_3)_2 \cdot 2H_2O$, were isolated from saturated solutions of $ZrO(NO_3)_2 \cdot nH_2O$ ($n = 2, 6$) or $ZrO(OH)(NO_3) \cdot 2H_2O$ in 70—100% HNO_3.[2] In the cited study, the $Zr(NO_3)_4 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ compositions were assigned to these precipitates, and the unit cell parameters of both compounds were determined. Evidence for the existence of the acidic salt $Zr(NO_3)_4 \cdot 2HNO_3 \cdot 4H_2O$ was reported;[3] however, the author pointed out a possible inaccuracy of the quantitative composition of zirconium nitrates associated with an unavoidable loss of nitric acid in the course of sampling and treatment of liquid and solid phases.

The $Zr(NO_3)_4$ salt can be prepared by the reaction of $ZrCl_4$ with an excess amount of nitric anhydride (nitrogen pentoxide) followed by sublimation of zirconium tetranitrate during heating of the reaction mixture *in vacuo*.[4] The sublimate can contain crystals of nitronium pentanitratozirconate $(NO_2)[Zr(NO_3)_5]$. The latter is the only zirconium(IV) nitrate complex whose crystal structure has been unambiguously established. In this compound, the Zr^{IV} atom is bound to five bidentate nitrate groups and has a coordination number of 10, which has not been observed earlier for zirconium.[5] The sublimate prepared according to an analogous procedure was recrystallized from nitroethane. This made it possible to isolate crystals whose compositions were detertmined by Raman spectroscopy and X-ray diffraction:[6] $(NO)_{3/4}(NO_2)_{1/4}[Zr(NO_3)_5]$ and $(NO)_{1/2}(NO_2)_{1/2}[Zr(NO_3)_5]$. However, earlier we have demonstrated[5] that the X-ray data processing performed in the study[6] was insufficiently accurate to draw reliable conclusions about the compositions of the compounds synthesized.

The nitratometallate anions can be present in complexes containing various single-charged cations. For example, the iron nitrate complexes $(Ph_4As)[Fe(NO_3)_4]$,[7] $(NO)_3[Fe(NO_3)_4]_2(NO_3)$,[8] $(NO_2)[Fe(NO_3)_4]$,[5] and $Cs[Fe(NO_3)_4]$ [9] contain the $[Fe(NO_3)_4]^-$ anions. Taking into account the formation of nitronium pentanitratozirconate $(NO_2)[Zr(NO_3)_5]$,[5] pentanitratozirconates with other cations would be expected to occur.

In the present study, we prepared four zirconium(IV) nitrate complexes and characterized them by X-ray

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diffraction analysis. In one of these complexes, $(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$ (**1**), the Zr atom is coordinated by water molecules and nitrate groups. Three other complexes, *viz.*, $Cs[Zr(NO_3)_5]$ (**2**), $(NH_4)[Zr(NO_3)_5](HNO_3)$ (**3**), and $(NO_2)_{0.23}(NO)_{0.77}[Zr(NO_3)_5]$ (**4**), contain the penatanitratozirconate anion.

Results and Discussion

The quantitative compositions of zirconium nitrate complexes **1**—**4** were determined by X-ray diffraction. A comparison of the experimental X-ray diffraction patterns of polycrystalline samples with those constructed from the results of X-ray diffraction analysis demonstrated that compounds **1** and **4** were prepared as single-phase samples (crystallization from nitric acid solutions of zirconyl nitrate in the presence of H_2SO_4 (run *1*, see the Experimental section) or P_2O_5 (run *4*), respectively. Crystallization from nitric acid solutions of $ZrO(NO_3)_2$ over H_2SO_4 in the presence of excess amounts of $CsNO_3$ or NH_4NO_3 (runs *2* and *3*, respectively) afforded precipitates containing cesium or ammonium nitrates along with phases **2** and **3**. The main crystallographic parameters and details of structure refinement are given in Table 1. Selected bond lengths are listed in Table 2.

The $(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$ compound (**1**), which was prepared by crystallization from a nitric acid solution of zirconyl nitrate over sulfuric acid, contains water molecules and nitronium cations (NO_2^+). The presence of these particles in a nitric acid solution is accounted for by dissociation of the acid according to the reaction

$$2\ HNO_3 = H_2O + NO_2^+ + NO_3^-, \qquad (1)$$

the degree of dissociation of pure HNO_3 being 3%.[10] If a solution contains metal cations, which bind water molecules to form stable complexes, the equilibrium (1) is shifted to the right. The presence of sulfuric acid as the drying agent does not exclude the possibility of the formation of nitrate hydrates.[11] The possibility of crystallization from a nitric solution of nitronium derivatives was confirmed in the study,[12] where fuming HNO_3 was used as the solvent for recrystallization of nitronium tetranitratoaurate $(NO_2)[Au(NO_3)_4]$.

Compound **1** contains the $[Zr(NO_3)_3(H_2O)_3]^+$ complex cations, in which the zirconium atom is coordinated by three water molecules and three bidentate nitrate groups (Fig. 1) and has a coordination number of 9. The coordination polyhedron is a distorted tricapped trigonal prism. The H_2O molecules occupy the vertices of one of the bases (Zr—O(6), 2.207 Å), and the oxygen atoms of the bidentate $N(1)O_3$ groups occupy one vertex in the equatorial plane (Zr—O(2), 2.256 Å) and one vertex in another base (Zr—O(1) 2.263 Å). These structures are typical of complexes containing three bidentate and three monodentate ligands.[13] In the crystal structures of the corresponding trihydrates,[14] the complex molecules $M(NO_3)_3(H_2O)_3$ (M = Yb, Tl) have similar structures. The nitrate groups in compound **1** exist as virtually sym-

Table 1. Crystallographic characteristics and details of X-ray diffraction study of $(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$ (**1**), $Cs[Zr(NO_3)_5]$ (**2**), $(NH_4)[Zr(NO_3)_5](HNO_3)$ (**3**), and $(NO_2)_{0.23}(NO)_{0.77}[Zr(NO_3)_5]$ (**4**)

Parameter	**1**	**2**	**3**	**4**
M/g mol^{-1}	894.64	534.18	482.33	434.99
Crystal system	Hexagonal	Monoclinic	Orthorhombic	Tetragonal
Space group	$P\bar{3}c1$	$P2_1/n$	$Pna2_1$	$I4_1/a$
a/Å	10.292(2)	7.497(1)	14.852(4)	13.675(3)
b/Å	10.292(2)	11.567(2)	7.222(2)	13.675(3)
c/Å	14.850(3)	14.411(3)	13.177(3)	25.489(5)
β/deg	90	96.01(2)	90	90
V/Å^3	1362.2(5)	1242.8(4)	1413.4(6)	4767(2)
Z	2	4	4	16
d_{calc}/g cm^{-3}	2.181	2.855	2.267	2.425
μ(Mo-K$_\alpha$)/mm^{-1}	0.922	3.874	0.904	1.046
Crystal dimensions/mm	0.3x0.4x0.4	0.2x0.3x0.5	0.3x0.4x0.6	0.7x0.7x0.8
T/K	180(2)	170(2)	170(2)	160(2)
θ$_{max}$/deg	27.84	28.00	26.02	28.99
Number of measured/independent reflections	10055/1089	4728/2986	2907/2780	2546/2488
Number of reflections with $F^2>2\sigma(F^2)$	759	2607	2423	2224
Number of reflections/parameters in least-squares	917/80	2774/200	2780/247	2488/217
wR_2/R_1	0.0775/0.0282	0.0527/0.0229	0.0689/0.0393	0.0568/0.0254

Table 2. Selected bond lengths (d) in the structures of **1—4**

Bond	d/Å	Bond	d/Å
$(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$ (**1**)			
Zr—O(1)	2.263(2)	N(1)—O(1)	1.283(4)
Zr—O(2)	2.256(2)	N(1)—O(2)	1.294(3)
Zr—O(6)	2.207(2)	N(1)—O(3)	1.198(3)
		N(2)—O(4)	1.262(4)
		N(2)—O(5)	1.250(3)
		N(3)—O(7)	1.104(8)
$Cs[Zr(NO_3)_5]$ (**2**)			
Zr—O(1)	2.303(2)	N(2)—O(4)	1.300(3)
Zr—O(2)	2.283(2)	N(2)—O(5)	1.261(3)
Zr—O(4)	2.244(2)	N(2)—O(6)	1.204(3)
Zr—O(5)	2.407(2)	N(3)—O(7)	1.279(3)
Zr—O(7)	2.249(2)	N(3)—O(8)	1.286(3)
Zr—O(8)	2.260(2)	N(3)—O(9)	1.197(3)
Zr—O(10)	2.277(2)	N(4)—O(10)	1.287(3)
Zr—O(11)	2.276(2)	N(4)—O(11)	1.279(3)
Zr—O(13)	2.246(2)	N(4)—O(12)	1.205(3)
Zr—O(14)	2.336(2)	N(5)—O(13)	1.292(3)
N(1)—O(1)	1.268(3)	N(5)—O(14)	1.280(3)
N(1)—O(2)	1.292(3)	N(5)—O(15)	1.198(3)
N(1)—O(3)	1.205(3)		
$NH_4[Zr(NO_3)_5](HNO_3)$ (**3**)			
Zr—O(1)	2.370(4)	N(2)—O(4)	1.262(6)
Zr—O(2)	2.237(4)	N(2)—O(5)	1.297(6)
Zr—O(4)	2.250(4)	N(2)—O(6)	1.198(6)
Zr—O(5)	2.280(4)	N(3)—O(7)	1.251(7)
Zr—O(7)	2.415(4)	N(3)—O(8)	1.288(7)
Zr—O(8)	2.260(4)	N(3)—O(9)	1.226(7)
Zr—O(10)	2.275(4)	N(4)—O(10)	1.294(7)
Zr—O(11)	2.272(4)	N(4)—O(11)	1.287(7)
Zr—O(13)	2.247(4)	N(4)—O(12)	1.185(7)
Zr—O(14)	2.260(4)	N(5)—O(13)	1.302(6)
		N(5)—O(14)	1.282(6)
N(1)—O(1)	1.267(6)	N(5)—O(15)	1.192(6)
N(1)—O(2)	1.296(6)	N(6)—O(16)	1.221(7)
N(1)—O(3)	1.201(5)	N(6)—O(17)	1.206(7)
		N(6)—O(18)	1.371(6)
$(NO_2)_{0.23}(NO)_{0.77}[Zr(NO_3)_5]$ (**4**)			
Zr—O(1)	2.250(2)	N(2)—O(4)	1.287(3)
Zr—O(2)	2.269(2)	N(2)—O(5)	1.284(2)
Zr—O(4)	2.280(2)	N(2)—O(6)	1.201(3)
Zr—O(5)	2.280(2)	N(3)—O(7)	1.282(3)
Zr—O(7)	2.284(2)	N(3)—O(8)	1.286(3)
Zr—O(8)	2.273(2)	N(3)—O(9)	1.198(3)
Zr—O(10)	2.373(2)	N(4)—O(10)	1.281(3)
Zr—O(11)	2.239(2)	N(4)—O(11)	1.294(3)
Zr—O(13)	2.273(2)	N(4)—O(12)	1.199(3)
Zr—O(14)	2.354(2)	N(5)—O(13)	1.296(3)
		N(5)—O(14)	1.271(3)
N(1)—O(1)	1.285(3)	N(5)—O(15)	1.195(3)
Zr—O(2)	1.285(3)		
Zr—O(3)	1.192(3)		

metrical bidentate ligands, whereas the equatorial O atoms in the above-mentioned structures of trihydrates are located at larger distances.

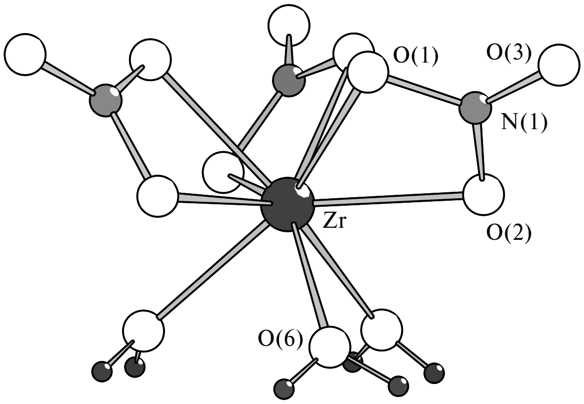

Fig. 1. Structure of the $[Zr(NO_3)_3(H_2O)_3]^+$ complex cation.

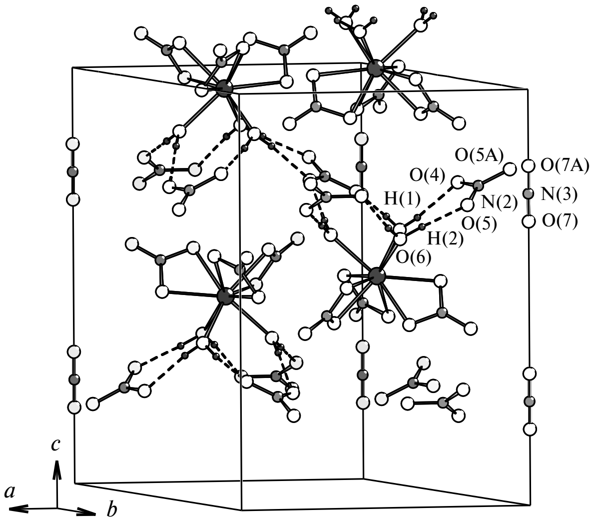

Fig. 2. Crystal structure of the $(NO_2)[Zr(NO_3)_3(H_2O)_3]_2(NO_3)_3$ complex. Some atoms present in the unit cell are omitted for clarity.

In the crystal structure of **1**, the complex cations form layers parallel to the (001) plane. These layers alternate with layers consisting of NO_2^+ cations and $N(2)O_3^-$ anions, which are not directly bound to the Zr atom (Fig. 2). Each nitrate anion links two $[Zr(NO_3)_3(H_2O)_3]^+$ complex cations belonging to different layers and forms four hydrogen bonds, O(6)—H(1)...O(4) and O(6)—H(2)...O(5) (O...O, 2.73 and 2.71 Å, respectively), with water molecules involved in the coordination environment of the zirconium atom.

The linear nitronium cations $N(3)O_2^+$ lie on threefold axes. The N—O distances (1.104(8) Å) are typical of this cation. In the structurally characterized $NO_2[Fe(NO_3)_4]$ and $NO_2[Zr(NO_3)_5]$ salts,[5] the N—O distances in the nitronium cations vary from 1.08 to 1.13 Å (aver., 1.11 Å). Each nitronium cation is surrounded by three nitrate anions in such a way that the nitrogen atoms of the cations and anions are in a single plane, whereas the O(5) atoms of the nitrate groups are located above and below this plane due to involvement in hydrogen bonding. Each nitronium cation forms six N(3)...O(5)—N(2)O_2 contacts (2.68 Å) and three O(7)...O(5)—N(2)O_2 contacts (2.68 Å) involving both oxygen atoms. In addition, the O(7) atoms of the nironium cations each form three O(7)...O(3)—N(1)O_2 bonds (2.86 Å) with the nitrate groups from the coordination environment of three $[Zr(NO_3)_3(H_2O)_3]^+$ complex cations. An analogous arrangement of the nitrate anions about the NO_2^+ cation was observed in the crystal structure of nitrogen pentoxide N_2O_5.[15]

The structure of complex **1** was confirmed by the IR spectrum, which shows vibrations at 570 cm^{-1} belonging to the NO_2^+ cation and a characteristic broad absorption band at 3500 cm^{-1} assigned to H_2O molecules. The bands with the vibrational frequencies $\nu_{as} = 1298$ cm^{-1} and $\nu_s = 1016$ cm^{-1} belong to the NO_3^- anion and the band at 848 cm^{-1} corresponds to the nitrate anion, which is not coordinated to the Zr atom.

A comparison of the results obtained in our study with those published earlier[2] shows that the authors of the study[2] have also synthesized compound **1**, which they erroneously described as $Zr(NO_3)_4 \cdot 6H_2O$. The fact that this is the same compound is evidenced by the similarity of both the unit cell parameters of their crystal lattices ($a = 10.28$, $c = 14.65$ Å, $V = 1341$ Å^3)[2] and the X-ray diffraction patterns of polycrystalline samples and is also supported by the fact that both compounds were prepared according to analogous procedures giving rise to crystals, which were similar in shape. In addition, the zirconium content calculated for **1** is consistent with the experiment.[2]

In spite of the similar conditions of the synthesis of the first three complexes (crystallization from nitric acid solutions over H_2SO_4), the structures of compounds **2** and **3** have no water molecules and contain the $[Zr(NO_3)_5]^-$ anions instead of the $[Zr(NO_3)_3(H_2O)_3]^+$ cations. This is evidence for similar thermodynamic stability of the complex zirconium nitrate ions $[Zr(NO_3)_3(H_2O)_3]^+$ and $[Zr(NO_3)_5]^-$, and, hence, the equilibrium (2) can be shifted to either the left or the right.

$$[Zr(OH)_2(NO_3)_2]_n \underset{H_2O}{\overset{H^+,\ NO_3^-}{\rightleftarrows}}$$

$$\rightleftarrows [Zr(NO_3)_3(H_2O)_3]^+ \underset{H_2O}{\overset{H^+,\ NO_3^-}{\rightleftarrows}} [Zr(NO_3)_5]^- \qquad (2)$$

In runs *2* and *3*, the presence of an excess amount of cesium or ammonium nitrate, respectively, led to the displacement of the water molecules from the inner sphere of zirconium(IV) triaqua trinitrate with nitrate anions.

Earlier, it has been demonstrated[9] that the use of P_2O_5 as the drying agent possessing higher dehydrating ability results not only in removal of water from the starting solution but also in accumulation of nitrogen pentoxide (nitric anhydride) N_2O_5 and the product of its partial decomposition, *viz.*, N_2O_4. Dissociation of nitrogen oxides to the NO^+, NO_2^+, and NO_3^- ions results in the shift of the equilibrium (1) to the left, and the presence of excess nitrate anions facilitates the displacement of the water molecules from the inner sphere of the complex to give the $(NO_2)_{0.23}(NO)_{0.77}[Zr(NO_3)_5]$ compound (**4**).

Compounds **2—4**, like the $(NO_2)[Zr(NO_3)_5]$ complex studied earlier,[5] contain the pentanitratozirconate anions $[Zr(NO_3)_5]^-$, in which the Zr^{IV} atom is coordinated by five bidentate nitrate groups and has an unusually high coordination number of 10. The coordination polyhedron of the Zr^{IV} atom is a bicapped square antiprism. This coordination polyhedron in which two nitrate groups occupy simultaneously two capping positions and two vertices of one lateral edge of the square antiprism is called the *cis* isomer of the tetragonal bicapped antiprism and is the most stable form of complexes containing five bidentate ligands[13] (Fig. 3). The Zr—O distances in the $[Zr(NO_3)_5]^-$ anions determined by X-ray diffraction vary from 2.233 to 2.415 Å (aver., 2.289 Å). The capping oxygen atoms are located at larger distances (Zr—O, 2.336—2.415 Å; aver., 2.375 Å). Based on the effective radius of the O^{2-} anion (1.21 Å for the coordination number of 2 and 1.22 Å for the coordination number of 3),[16] we found that the previously unknown effective ionic radius of Zr^{IV} (coordination number is 10) is 1.075 Å.

The formation of the structurally similar pentanitratometallate anions $[Ln(NO_3)_5]^{2-}$ is typical of rare-earth metals of the yttrium subgroup.[14] The geometry of the $[Zr(NO_3)_5]^-$ and $[Ln(NO_3)_5]^{2-}$ anions can alternatively be described as a trigonal-bipyramidal arrangement of the N atoms of the bidentate nitrate groups about the complex-forming atom.[5] The planes of the axial NO_3 groups are twisted with respect to each other by approximately 90°. Two equatorial nitrate groups are twisted in one direction, whereas the third equatorial nitrate group

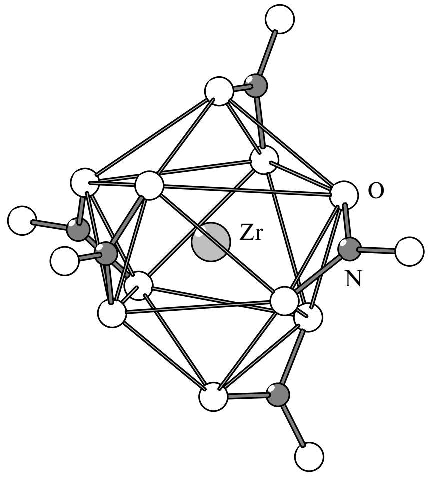

Fig. 3. Representation of the structure of the $[Zr(NO_3)_5]^-$ anion present in compounds **2**, **3**, and **4** as a bicapped square antiprism.

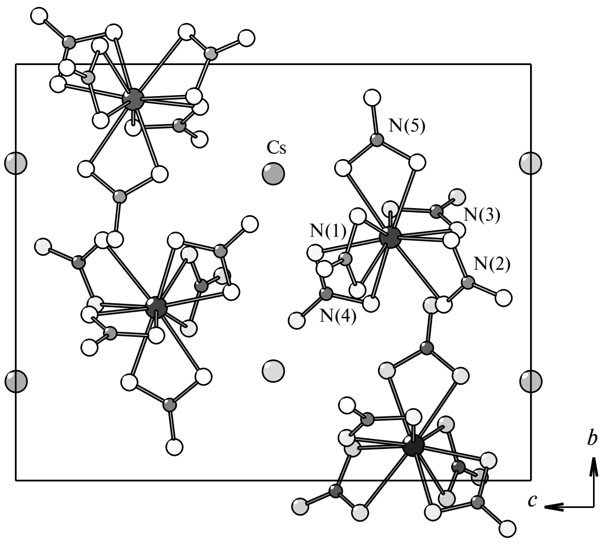

Fig. 4. Crystal structure of Cs[Zr(NO_3)$_5$] projected onto the 0*yz* plane.

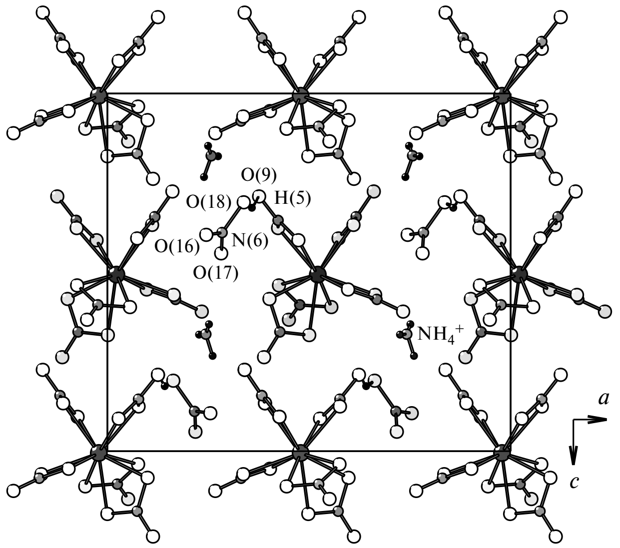

Fig. 5. Crystal structure of (NH_4)[Zr(NO_3)$_5$](HNO_3) projected along the *b* axis.

is twisted in the opposite direction. Due to a smaller effective ionic radius of the Zr atom in the $[Zr(NO_3)_5]^-$ anion compared to the radius of Ln in $[Ln(NO_3)_5]^{2-}$, the nitrate groups are twisted with respect to the equatorial plane by a somewhat larger angle.[5] This tendency is observed for all known pentanitratozirconate anions. Evidently, the $[Zr(NO_3)_5]^-$ anion is rather stable, and it is a typical nitrate complex anion for the crystal chemistry of Zr^{IV}. The structure of this anion depends slightly on the nature of the counterion and various packing effects.

The island structure of compound **2** consists of the $[Zr(NO_3)_5]^-$ complex anions and cesium cations (Fig. 4). Each Cs^+ cation is surrounded by five $[Zr(NO_3)_5]^-$ anions and forms seven Cs...O contacts (3.088—3.313 Å) with the NO_3 groups involved in these anions. Each anion, in turn, is surrounded by five Cs^+ cations occupying the vertices of a strongly distorted square pyramid.

The $(NH_4)[Zr(NO_3)_5](HNO_3)$ compound (**3**) contains neutral HNO_3 molecules. This structural feature of **3** is attributable to a small size of the ammonium cation, which cannot provide a sufficiently large distance between the pentanitratozirconate anions. Each nitric acid molecule forms the O(18)—H...O(9)—[NO_2] hydrogen bond with the nitrate group involved in the coordination environment of the Zr^{IV} atom (O...O, 2.79 Å) (Fig. 5).

The structure of the $(NO_2)_{0.23}(NO)_{0.77}[Zr(NO_3)_5]$ complex (**4**) is isotypical to nitronium pentanitratozirconate $(NO_2)[Zr(NO_3)_5]$ studied earlier.[5] In the latter compound, approximately three-fourth of the nitronium ions are replaced by nitrosonium cations. It should be noted that the nitrogen atoms of the NO_2^+ and NO^+ cations occupy virtually the same crystallographic position, resulting in a decrease in the unit cell volume by 223.8 Å (or by 14 Å per structural unit). This result is consistent with the difference in the effective volumes of the NO_2^+ and NO^+ cations (according to our evaluation,[5] this difference is 10 Å).

In complex **4**, each nitronium (nitrosonium) cation is surrounded by five $[Zr(NO_3)_5]^-$ anions located at the vertices of a strongly distorted square pyramid and forms four N(cation)...O(anion) contacts and nine O(cation)...O(anion) contacts (2.50 and 2.84 Å, respectively).

Apparently, compound **4** has been prepared earlier.[6] However, the data on the compositions and structures of the samples were not reliable because of insufficiently accurate X-ray data processing. Nevertheless, the presence of the NO^+ and NO_2^+ cations in these compounds was confirmed by Raman spectroscopy based on the characteristic lines at 2300 and 1396 cm^{-1}, respectively. In the IR spectrum of complex **4** prepared in the present study, the absorption bands at 2273 and 570 cm^{-1} correspond to the nitrosonium and nitronium cations, respectively. The absence of an absorption band at 1400 cm^{-1} (NO_2^+) is attributable to the fact that the corresponding vibration is symmetrically linear and does not change the dipole moment.

The mononuclear nitrate complex cations and anions, $[Zr(NO_3)_3(H_2O)_3]^+$ and $[Zr(NO_3)_5]^-$, prepared by crystallization from nitric acid solutions of zirconyl nitrate are compositionally and structurally similar to the ionic and molecular complexes, $[Ln(NO_3)_5]^{2-}$ and $[Ln(NO_3)_3(H_2O)_3]$, but are characterized by a smaller M—O bond length, resulting in an increase in repulsion between the ligands, which is compensated by an increase in the positive charge on the central atom.

Experimental

Synthesis of compounds 1—4. Zirconyl nitrate hydrate (zirconium dinitrate oxide) $ZrO(NO_3)_2 \cdot 2H_2O$ of reagent grade (2 g) was dissolved under magnetical stirring for one day in 100% HNO_3 (10 mL), which was prepared according to a known procedure.[17] The resulting solution was divided into four equal portions, which were used in subsequent experiments. In run *1*, the solution was placed in a desiccator containing concentrated H_2SO_4 as the drying agent. In runs *2* and *3*, a threefold molar excess of cesium nitrate (1.1 g) or ammonium nitrate (0.45 g), respectively, was added to the starting solution and the mixture was stored over H_2SO_4. In run *4*, the starting solution was kept in a desiccator over phosphorus pentoxide. After one week, crystallization started, and the liquid phase was completely removed after 2—4 weeks. In runs *1—4*, air-unstable crystalline precipitates of compounds **1—4**, respectively, were obtained.

IR spectra of compounds **1** and **4** were recorded on a PE-1600 FTIR Fourier-transform spectrometer. Samples were ground in a dry box, mixed with Nujol, and sealed in polyethylene bags because compounds **1** and **4** are unstable in air and interact with the material of plates (KBr). IR of **1** (Nujol mull), ν/cm^{-1}: 3500 (H_2O); 2342; 2022; 1928; 1640 (NO_3^-); 1298 (NO_3^-); 1058; 1016 (NO_3^-); 848 (NO_3^-); 792 (NO_3^-); 766; 570 (NO_2^+); 522; 440; 418. IR of **4** (Nujol mull), ν/cm^{-1}: 2273 (NO^+); 2025; 1610 (NO_3^-); 1460; 1376 (NO_2^+); 1300; 730; 720; 570 (NO_2^+).

Powder X-ray diffraction analysis of polycrystalline samples was carried out on a STADI/P (Stoe) diffractometer equipped with a position-sensitive detector (Cu-Kα radiation, Ge monochromator). Samples were ground in a dry box and placed between polystyrene films wetted with Vaseline oil to prevent them from atmospheric moisture. The phases were identified using the PCPDFWIN database.[18] The powder X-ray diffraction pattern of a polycrystalline sample of **1** corresponds to the X-ray pattern, which was assigned[18] to the $Zr(NO_3)_4 \cdot 6H_2O$ compound based on the results of the study.[2] The powder X-ray diffraction pattern of a polycrystalline sample of **4** agrees well with that calculated for nitronium pentanitratozirconate[5] $(NO_2)[Zr(NO_3)_5]$, which has been studied earlier by X-ray diffraction, and it was identified with slightly smaller unit cell parameters.

Single-crystal X-ray diffraction study of complex **1** was carried out on a diffractometer equipped with a IPDS (Stoe) 2D detector. Single-crystal X-ray diffraction studies of compounds **2—4** were performed on a four-circle STADI-4 (Stoe) diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). Single crystals were selected under a layer of Vaseline oil or in a dry box using a polarizing microscope. The crystals were sealed in thin-walled glass capillaries. All structures were solved by direct methods followed by calculations of Fourier syntheses with the use of the SHELXS-97[19] and SHELXL-97[20] program packages. The structures were refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms in the structures of **1** and **3** were localized from difference Fourier syntheses and refined isotropically. For the crystal structure of **2**, the empirical absorption correction was applied using the psi-scan method. Complete crystallographic parameters for the structures of **1—4** were deposited at the Fachinformationszentrum (FIZ) Karlsruhe; the registry numbers are 414546—414549, respectively.

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