Synthesis and crystal structures of zirconium(IV) nitrate complexes
(NO$_2$)[Zr(NO$_3$)$_3$(H$_2$O)$_3$]$_2$(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$_2$O)$_3$]$_2$(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 crys-
tallization from nitric acid solutions in the presence of H$_2$SO$_4$ or P$_2$O$_5$. 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$_2$O)$_3$]$^+$ 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, com-
plex 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$_2^+$, 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 coordina-
tion 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 com-
plexes were known, which is associated with the fact that
these complexes are highly prone to hydrolysis giving rise to
tizirconyl derivatives. For example, zirconyl nitrate hy-
drate ZrO(NO$_3$)$_2$·2H$_2$O 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 crystalli-
zation water molecules.\footnote{1} Crystalline precipitates, which
decomposed in air to form ZrO(NO$_3$)$_2$·2H$_2$O, were
isolated from saturated solutions of ZrO(NO$_3$)$_2$·nH$_2$O
(n = 2, 6) or ZrO(OH)(NO$_3$)·2H$_2$O in 70—100% HNO$_3$.\footnote{2}
In the cited study, the Zr(NO$_3$)$_4$·6H$_2$O and Zr(NO$_3$)$_3$·
5H$_2$O 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$_3$)$_4$·2HNO$_3$·4H$_2$O was reported;\footnote{3} however, the au-
thor pointed out a possible inaccuracy of the quantitative
composition of zirconium nitrates associated with an un-
avoidable 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 (nitro-
gen pentoxide) followed by sublimation of zircon-
ium tetranitrate during heating of the reaction mixture
in vacuo.\footnote{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 num-
ber of 10, which has not been observed earlier for zir-
conium.\footnote{5} The sublimate prepared according to an analo-
gous procedure was recrystallized from nitroethane. This
made it possible to isolate crystals whose composi-
tions were determined by Raman spectroscopy and
X-ray diffraction;\footnote{6} (NO$_3$)$_3$(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\footnote{5} that the X-ray data processing performed
in the study\footnote{6} was insufficiently accurate to draw reliable
conclusions about the compositions of the compounds
synthesized.

The nitratometallate anions can be present in com-
plexes containing various single-charged cations. For ex-
ample, the iron nitrate complexes (Ph$_4$As)[Fe(NO$_3$)$_4$],\footnote{7}
(NO$_3$)$_3$[Fe(NO$_3$)$_3$](NO)$_2$,\footnote{8} (NO$_2$)[Fe(NO$_3$)$_4$],\footnote{5} and
Cs[Fe(NO$_3$)$_4$] contain the [Fe(NO$_3$)$_4$]$^-$ anions. Taking
into account the formation of nitronium pentanitrato-
zirconate (NO$_2$)[Zr(NO$_3$)$_5$],\footnote{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
diffraction analysis. In one of these complexes, \((\text{NO}_2)[\text{Zr(NO}_3)_3(\text{H}_2\text{O})_3]_2\text{NO}_3\) (1), the Zr atom is coordinated by water molecules and nitrate groups. Three other complexes, viz., \(\text{Cs[Zr(NO}_3)_5]\) (2), \((\text{NH}_4)[\text{Zr(NO}_3)_5(\text{HNO}_3)]\) (3), and \((\text{NO}_2)_{0.23}\text{NO}_{0.77}[\text{Zr(NO}_3)_5]\) (4), contain the pentanitratozirconate 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\(_2\text{SO}_4\) (run 1, see the Experimental section) or P\(_2\text{O}_5\) (run 4), respectively. Crystallization from nitric acid solutions of ZrO(NO\(_3\))\(_2\) over H\(_2\text{SO}_4\) in the presence of excess amounts of CsNO\(_3\) or NH\(_4\)NO\(_3\) (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 \((\text{NO}_2)[\text{Zr(NO}_3)_3(\text{H}_2\text{O})_3]_2\text{NO}_3\) 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

\[
2 \text{HNO}_3 = \text{H}_2\text{O} + \text{NO}_2^+ + \text{NO}_3^-, \tag{1}
\]

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 tetranitratourate (NO\(_2\))[Au(NO\(_3\))]\(_4\).

Compound 1 contains the \([\text{Zr(NO}_3)_5(\text{H}_2\text{O})_3]^+\) 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.

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