Synthesis and crystal structures of zirconium(IV) nitrate complexes 
(NO₂)[Zr(NO₃)₃(H₂O)₃]₂(NO₃)₃, Cs[Zr(NO₃)₅], and (NH₄)[Zr(NO₃)₅](HNO₃)

I. V. Morozov,* A. A. Fedorova, D. V. Palamarchuk, and S. I. Troyanov

Department of Chemistry, M. V. Lomonosov Moscow State University, 
1 Leninskie Gory, 119992 Moscow, Russian Federation.
E-mail: morozov@inorg.chem.msu.ru

The zirconium nitrate complexes (NO₂)[Zr(NO₃)₃(H₂O)₃]₂(NO₃)₃ (1), Cs[Zr(NO₃)₅] (2), 
(NH₄)[Zr(NO₃)₅](HNO₃) (3), and (NO₂)₀.₂₃(NO)₀.₇₇[Zr(NO₃)₅] (4) were prepared by crys-
tallization from nitric acid solutions in the presence of H₂SO₄ or P₂O₅. The complexes were 
characterized by X-ray diffraction. The crystal structure of 1 consists of nitrate anions, nitronium 
cations, and [Zr(NO₃)₃(H₂O)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 
ZrIV atom is a tricapped trigonal prism formed by nine oxygen atoms. The island structures of 
2 and 3 contain [Zr(NO₃)₅]⁻ anions and Cs⁺ or NH₄⁺ cations, respectively. In addition, com-
plex 3 contains HNO₃ molecules. Complex 4 differs from (NO₂)[Zr(NO₃)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(NO₃)₅]⁻ anion involved in complexes 2—4, the 
ZrIV 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 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 hy-
drate ZrO(NO₃)₂•2H₂O generally crystallizes from nitric acid solutions. The crystal structure of this compound 
consists of the infinite OH-bridged [Zr(NO₃)₂(OH)₂]ₙ chains, which are linked to each other through crystalli-
zation water molecules.¹ Crystalline precipitates, which 
decomposed in air to form ZrO(NO₃)₂•2H₂O, were iso-
lated from saturated solutions of ZrO(NO₃)₂•nH₂O 
(n = 2, 6) or ZrO(OH)(NO₃)•2H₂O in 70—100% HNO₃.² 
In the cited study, the Zr(NO₃)₄•6H₂O and Zr(NO₃)₄• 
•5H₂O 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(NO₃)₄•2HNO₃•4H₂O was reported,³ however, the author 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(NO₃)₄ salt can be prepared by the reaction of 
ZrCl₄ 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.⁴ The sublimate can contain crystals of 
nitronium pentanitratozirconate (NO₂)[Zr(NO₃)₅]. The latter is the only zirconium(IV) nitrate complex whose 
crystal structure has been unambiguously established. In this compound, the ZrIV 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.⁵ The sublimate prepared according to an analo-
gous procedure was recrystallized from nitroethane. This 
made it possible to isolate crystals whose compositions 
were determined by Raman spectroscopy and X-ray diffraction:⁶ (NO₃)₀.₃₅(NO₂)₀.₆₅[Zr(NO₃)₅] and 
(NO₃)₀.₂₅(NO₂)₀.₇₅[Zr(NO₃)₅]. However, earlier we have demonstrated⁸ that the X-ray data processing performed 
in the study⁶ 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 (Ph₄As)[Fe(NO₃)₄],⁷ 
(NO₃)₂[Fe(NO₃)₄],⁸ (NO₃)₂[Fe(NO₃)₄],⁵ and 
Cs[Fe(NO₃)₄]² contain the [Fe(NO₃)₄]⁻ anions. Taking 
into account the formation of nitronium pentanitrato-
zirconate (NO₂)[Zr(NO₃)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
diffraction analysis. In one of these complexes, 
(NO2)[Zr(NO3)3(H2O)3]2(NO3)3 (1), the Zr atom
is coordinated by water molecules and nitrate groups.
Three other complexes, viz., Cs[Zr(NO3)5] (2),
(NH4)2[Zr(NO3)3][HNO3] (3), and
(NO2)0.23(NO)0.77[Zr(NO3)3] (4), contain the penat-
nitratozirconate 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 pat-
terns 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 H2SO4 (run 1, see the
Experimental section) or P2O5 (run 4), respectively. Crys-
tallization from nitric acid solutions of ZrO(NO3)2 over
H2SO4 in the presence of excess amounts of CsNO3 or
NH4NO3 (runs 2 and 3, respectively) afforded precipi-
tates 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. Se-
lected bond lengths are listed in Table 2.

The (NO2)[Zr(NO3)3(H2O)3]2(NO3)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 (NO2+). The pres-
cence of these particles in a nitric acid solution is ac-
counted for by dissociation of the acid according to the
reaction

\[ 2 \text{HNO}_3 = \text{H}_2\text{O} + \text{NO}_2^+ + \text{NO}_3^- , \]
the degree of dissociation of pure HNO3 being 3%. If a
solution contains metal cations, which bind water mol-
ecules 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 forma-
tion of nitrate hydrates.11 The possibility of crystallization
from a nitric solution of nitronium derivatives was con-
firmed in the study,12 where fuming HNO3 was used as
the solvent for recrystallization of nitronium tetranitrato-
aurate (NO2)[Au(NO3)4].

Table 1. Crystallographic characteristics and details of X-ray diffraction study of (NO2)[Zr(NO3)3(H2O)3]2(NO3)3 (1),
Cs[Zr(NO3)5] (2), (NH4)2[Zr(NO3)3][HNO3] (3), and (NO2)0.23(NO)0.77[Zr(NO3)3] (4)

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