INTRODUCTION

Oxonitrate complexes of vanadium- and chromium-subgroup elements still haven’t been studied very well. However, nitrate complexes of $d$ elements are of undoubted interest due to their unusual structure and interesting chemical and physical properties. For example, atoms of transition metals in nitrate complexes form unusual polyhedra with high coordination numbers. Some anhydrous nitrates and nitrate complexes can pass to the gas phase without decomposition and act as oxidants and nitrating agents. For example, it was shown in [1] that VO(NO$_3$)$_3$ is a convenient nitrating agent that makes it possible to nitrate benzene derivatives with substituents of different natures at room temperature and at a high rate.

The insufficient study of oxonitrates of V and Cr subgroups is related to a great extent by the complexity of their synthesis and tendency to hydration and hydrolysis. For example, volatile and unstable oxonitrates MO$_2$(NO$_3$)$_3$ ($M = \text{Cr, Mo, W}$) were obtained for the first time in 1955 as products of the reaction of metal oxochlorides with nitrogen anhydride and the subsequent distillation of nitronium chloride in vacuum [2]. The structure of chromyl nitrate CrO$_2$(NO$_3$)$_2$ in the gas phase was established by gas electron diffraction using quantum-chemical calculations [3]. Molybdenyl nitrate was characterized as a viscous colorless liquid which becomes turbid in air due to hydrolysis; tungstyl nitrate exist as yellowish crystals. There are no new data (including structural) on these or other oxonitrates of chromium-subgroup elements [4].

Among the oxonitrate complexes of fifth-group $d$ elements, the best studied compounds are vanadium derivatives, whereas the only data on Nb and Ta oxonitrates can be found in [2], where oxonitrates MO(NO$_3$)$_3$ ($M = \text{V, Nb, Ta}$) were obtained by the reaction of N$_2$O$_5$ with oxochlorides of the corresponding metals. Gas electron diffraction analysis established that the vanadium atom in the vanadyl trinitrate molecule VO(NO$_3$)$_3$, has an unusually high coordination number (7); it coordinates one terminal O atom and three terminal bidentate NO$_3$ groups [5] with the formation of a polyhedron as a distorted octahedron. The vanadium atom forms a similar polyhedron in the complex with acetonitrile VO(NO$_3$)$_3$CH$_3$CN [6]. Along with mononuclear complexes, there are binuclear oxonitrates complexes (Ph$_4$As)$_2$[V$_2$O$_3$(NO$_3$)$_6$] and (Ph$_3$As)$_2$[V$_2$O$_3$(NO$_3$)$_2$Cl$_4$] [7], where V atoms are connected by bridge oxygen atoms and have a coordination number of 6.

Recently we significantly simplified the technique for synthesizing vanadyl trinitrate VO(NO$_3$)$_3$ and, for the first time, determined its structure in the solid and liquid phases by X-ray diffraction (XRD) and ab initio calculation, respectively. It was shown that VO(NO$_3$)$_3$ retains the molecular structure in the condensed state, exhibiting a coordination number of 7, which is fairly rare for V atoms [8]. We also confirmed the data in the literature, according to which VO(NO$_3$)$_3$ is an efficient...
and convenient nitrating agent [1], and showed that
the nitrination of naphthalene yields mono- and dinitro
derivatives.

Applying new approaches to the synthesis of
nitrination complexes of Cr- and V-subgroup elements
in the higher oxidation states allowed us to obtain,
along with VO(NO₃)₂, three new oxonitrate com-
plexes, Cs[VO₂(NO₃)₂], MoO₂(NO₃)₂, and
Cs[MnO₂(NO₃)₃], and establish their structure by the
XRD method. The structure of MoO₂(NO₃)₂ mole-
cules in the gas phase and solution was determined by
a nonempirical quantum-chemical calculation. The
results obtained are given below.

**EXPERIMENTAL**

We used the following agents (of a purity grade no
lower than chemically pure): V, H₂MoO₄, CsNO₃, and
P₂O₅. Anhydrous nitric acid was prepared according to
the technique described in [9].

To obtain Cs[VO₂(NO₃)₂] (I), a mixture of metallic
vanadium and cesium nitrate was dissolved in anhy-
drous nitric acid (molar ratio V : CsNO₃ : HNO₃ = 1 : 2 : 10). The solution was placed in a vacuum desiccator
above phosphoric anhydride. Two weeks later, the
solution volume decreased by a factor of about 5 and a
viscous red-orange mass was formed. Further expo-
sure above phosphoric anhydride for a week did not
lead to any changes in the reaction mixture; therefore,
P₂O₅ in the desiccator was replaced by solid sodium
hydroxide to remove the volatile residue of nitric acid
and nitrogen oxides from the reaction mass. An orange
eine-grained mass with traces of mother liquor was
formed two weeks later. To obtain crystals large enough
for XRD analysis, the mixture was sealed in a glass
ampoule and kept at about 50°C for a month; after this,
crystals of two types could be easily seen in the
sample: relatively large colorless crystals (according to
the X-ray phase analysis (XPA), acid cesium nitrate of
CsH(NO₃)₂ [10]), and small goldish crystals (phase I,
previously unknown, whose composition was deter-
mined by XRD).

To obtain a crystalline MoO₂(NO₃)₂ (II) sample,
excess anhydrous HNO₃ was added to a molybdenum
acid (H₂MoO₄) weight and the mixture was placed in
the vacuum desiccator above phosphoric anhydride.
Complete dissolution of the solid phase with the for-
mation of a bright yellow solution occurred not imme-
diately but only after seven days. Furthermore, the liq-
uid phase amount gradually decreased and colorless
crystals (which rapidly became turbid in air) began to
crystallize from the solution. The solution was com-
tpletely removed 15 days after placing the mixture in
the vacuum desiccator. The X-ray phase analysis
showed the presence of a new phase II, whose compo-
sition was established by XRD.

Cs[MoO₂(NO₃)₃] (III) crystals were grown simi-
larly to compounds II. Anhydrous nitric acid was
added to a mixture of crystalline H₂MoO₄ and CsNO₃
(molar ratio H₂MoO₄ : CsNO₃ : HNO₃ = 1 : 2 : 10). A
solution, like in the synthesis of II, was formed only
several days later. The exposure in the desiccator lasted
for about two weeks, up to the complete removal of the
liquid phase. In this case, colorless hygroscopic crys-
tals of two types were formed, differing in shape and
coloring in polarized light. Smaller crystals were found
to be a previously unknown phase whose composition
was established by XRD: Cs[MoO₂(NO₃)₃]. As in the
synthesis of compound I, the second phase was
CsH(NO₃)₂ [10].

To carry out XPA, hygroscopic samples were
grinded in a dry box, placed on a quartz holder, and
hermetically coated by a polystyrene film. The collect-
ung was performed on a DRON-3M diffractometer
(graphite monochromator, Kα radiation) in the range
of angles 2θ from 5° to 60°. The presence of previously
unknown phases in the samples was confirmed by
comparing the obtained X-ray diffraction patterns of
polycrystalline samples with the diffraction patterns
calculated on the basis of the XRD data for com-
ounds I—III.

Hygroscopic crystals of compounds I, II, and III
for single-crystal XRD were selected under a Vaseline
oil layer and checked for single crystallinity in a polar-
ized-light microscope. The selected single crystals
were placed in glass capillaries which were then sealed.
The collection was performed on an IPDS (STOE)
instrument (MoKα radiation, λ = 0.71073 Å, graphite
monochromator). All the structures were identified by
direct methods with subsequent Fourier syntheses
using the SHELX97 software package [11]. The struc-
ture data were deposited in the Inorganic Crystal
Structure Database (ICSD) with the numbers 421222,
421223, and 421224 for compounds I, II, and III,
respectively. The conditions of the XRD experiment
and the main crystallographic data on the structures
studied are listed in Table 1; some bond lengths and
bond angles for these structures are given in Table 2.
The structures were plotted using the Diamond pro-
gram for visualizing structural data [12].

**RESULTS AND DISCUSSION**

The synthesis method applied in this study was pre-
viously used to obtain anhydrous nitrates and metal-
nitrate Aₙ[M(NO₃)ₙ] complexes, where A is a monoval-
cation of alkali metal, ammonium, NO⁺, or
NO₂⁻ and M is a d metal in oxidation states of +2 (Mn,
Co, Ni, Cu), +3 (Cr), or +4 (Zr) (see, for example,
[13, 14]). This method does not require complex
instrumental equipment or the use of such corrosive
and unstable (in storage) reagents as N₂O₅, N₂O₃, and
anhydrous metal chlorides. The samples formed are