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Synthesis, Crystal Structure, and Properties of Triphenylguanidinium Perrhenate Hemihydrate

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Abstract—Triphenylguanidinium perrhenate hemihydrate, $[(C_6H_5NH)_3C]ReO_4 \cdot 0.5H_2O$ (**I**), is synthesized, and its crystal structure and some properties are studied. The colorless extended plate-like crystals of compound **I** are triclinic (space group $P\bar{1}$, $Z = 4$, 293 K, $a = 9.8716(17)$, $b = 14.093(2)$, $c = 15.439(3)$ Å, $\alpha = 99.632(9)°$, $\beta = 101.802(9)°$, $\gamma = 95.361(10)°$). Compound **I** has no isostructural analogs, and the conformations of both crystallographically independent triphenylguanidinium cations differ by a higher symmetry (C_{3h}) from those for cations of this type in all other structurally studied compounds. The following parameters are determined: the upper limit of the temperature stability of compound **I** (383 K), the melting point of anhydrous $[(C_6H_5NH)_3C]ReO_4$ (**Ia**) of 441 K, the enthalpy of dehydration of compound **I** ($\Delta H_{\rm dehydr}^{(383\ {\rm K})} =$ 10.0(8) kJ/mol), and the enthalpy of melting of anhydrous **Ia** ($\Delta H_{\rm m}^{(441\ {\rm K})} = 16.6(9)$ kJ/mol).

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INTRODUCTION

Triphenylguanidinium compounds find use in processes of concentrating of rare and scattered elements as flotation agents [1–3]. When rhenium-containing molybdenites are subjected to concentrating, rhenium transforms in air into the oxidized form (perrhenate) and can additionally be concentrated in the phase enriched in an organic flotation agent [3]. Numerous attempts to obtain these compounds as single crystals suitable for X-ray diffraction analysis were unsuccessful. A close analog of similar compounds, the triphenylguanidinium derivative with the pertechnetate anion, was described [4]; however, its structure was not determined. An uncertainty for the possible water content in the composition of both compounds was primarily caused by a smallness of this value. It was assumed that this could be adsorbed water or hydrate water but partially lost because the binding was weak. This water can exert a considerable effect on the thermal decomposition mechanism and solid thermolysis products formed [4]. In this work, we synthesized for the first time a single crystal of $[(C_6H_5NH)_3C]ReO_4 \cdot 0.5H_2O$ (**I**), studied its structure, and eliminated an uncertainty in the interpretation of the state of water in this compound. Some thermal properties important for the conversion of triphenylguanidinium perrhenate to metallic rhenium were studied, and the possibility of obtaining nanodispersed rhenium dispersed in amorphous carbon was demonstrated.

EXPERIMENTAL

Triphenylguanidinium chloride (high-purity grade), sulfuric acid (reagent grade), and potassium perrhenate were used.

Synthesis of compound I. Triphenylguanidinium chloride was dissolved in 5% sulfuric acid on heating (70°C), and $KReO_4$ (0.05 mol/L) was added dropwise to the obtained heated solution. A precipitate of compound **I** was formed almost instantly, rapidly sedimentated, and was pale pink. A small amount of low-quality crystals unsuitable for X-ray diffraction analysis was formed on cooling. Recrystallization with heating resulted in the formation of spherical glassy agglomerates. To obtain single crystals, the precipitate was separated from the solution by filtration on the Büchner funnel with the Millipore membrane (200 μm) and dissolved in an acetone–ethanol–water (1 : 1 : 1) mixture of solvents. The solution was very slowly (2 months) evaporated at ambient temperature. A portion of the formed crystals was suitable for X-ray diffraction analysis. The crystals were thin, long, and almost colorless plates.

Thermal studies. The obtained crystals were analyzed by differential thermal analysis (DTA) and thermal gravimetry (TG) on a Q1500 D derivatograph (MOM, Hungary). A series of studies was carried out with a scanning rate of 2.5 and 5 K/min in the temperature range from 293 to 800 K in argon with the blowing rate ranging from 14 to 25 L/h. Below 590 K the rate of blowing with argon does not affect the thermal effects, whereas at higher temperatures an oxygen

Table 1. Crystallographic data and experimental and refinement details for structure **I**

Parameter	Value
Formula weight	547.58
Space group	$P\bar{1}$
a, Å	9.8716(17)
b, Å	14.093(2)
c, Å	15.439(3)
α, deg	99.632(9)
β, deg	101.802(9)
γ, deg	95.361(10)
V, Å^3	2054.6(6)
Z	4
ρ_{calcd}, g/cm^3	2.555
μ, mm^{-1}	5.94
θ_{max}, deg	27.5
Index range h, k, l	$-12 \le h \le 12$, $-17 \le k \le 18$, $-19 \le l \le 20$
All reflections	19983
Independent reflections (N_1)	9296 (R_{int} = 0.0410)
Reflections with $I > 2\sigma(I)$ (N_2)	5538
Number of refined parameters	502
Goodness-of-fit	0.955
R_1 for N_2	0.0397
wR_2 for N_1	0.0863
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.20/−1.62
T_{min}/T_{max}	0.4660/0.6224

admixture in the atmosphere above the sample increases gradually and results in the gradual oxidation of the sample. Thermolysis and isothermal annealing were carried out in the range from 523 to 1273 K in an NTR-PRT-1000 instrument, which made it possible to detect the sign of the thermal effect of decomposition in the controlled atmosphere (argon or hydrogen) by the DTA method (using calibration by standard enthalpies of benzoic acid melting and the phase transition in potassium bichromate). The thermolysis products of anhydrous $[(C_6H_5NH)_3C]ReO_4$ (**Ia**) were also obtained by isothermal annealing at a specified temperature (in a current of argon or hydrogen) in a setup based on a quartz tubular electric furnace.

An analysis of carbon was performed on a Carlo-Erba NA 1500 elemental analyzer (Carlo Erba Strumentazione). Rhenium was determined on an AAnalyst 400 atomic absorption spectrometer (Perkin-Elmer).

The stability of rhenium carbide against laser evaporation was determined on a Lamma-1000 laser microanalyzer.

Powder diffraction patterns were recorded on a URD-63 diffractometer (Carl Zeiss) (CuK_α radiation, λ = 1.5418 Å).

X-ray diffraction analysis was carried out on a Bruker KAPPA APEX II four-circle automated diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) [5] at 293 K. Cell parameters were determined over the whole data array [6]. Absorption intensities were applied to experimental intensities using the SADABS procedure [7]. The structure was solved by a direct method (SHELXS-97) [8] and refined by full-matrix least squares for F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [8]. The hydrogen atoms bound to the C and N atoms were placed in geometrically calculated positions with the isotropic temperature factors equal to $1.2U_{eq}$(C, N). The hydrogen atoms of the water molecule were localized objectively and refined with imposing conditions of tending the distances O–H to 0.85(2) Å and H···H to 1.35(2) Å with the isotropic temperature factors equal to $1.5U_{eq}$(O). The crystallographic data and refinement parameters of the studied structure are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The coordinates of atoms were deposited with the Cambridge Crystallographic Data Centre (CCDC, no. 804362; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

No compounds isostructural to compound **I** were found in the CCDC. The crystal structure of compound **I** contains two independent formula units of triphenylguanidinium perrhenate (Fig. 1a). The cation of only one of them is linked with the water molecule, which determines the fractional hydrate number in the formula of compound **I**.

The CN_3 fragments of the triphenylguanidinium cations are planar (the maximum deviation for the C(1) atom is 0.0204(51) Å). The sums of the NCN angles at the C(1) and C(2) central atoms of two formula units are 359.9(6)° and 360.0(5)°, respectively. The ranges of the NCN angles are 119.4(6)°–121.1(6)° and 118.8(5)°–120.9(5)°, respectively. This is due to the sp^2 hybridization of the central carbon atom and the nitrogen atoms bound to this carbon atom, which is consistent with published data [9–17].

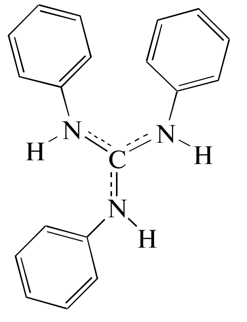
The average values of deviations of the CNCN torsion angles from ideal values of 180° and 0° for the cations with the C(1) and C(2) central atoms are 12.1(9)° and 17.0(9)°, respectively. In the second case, the larger value can be due to the strain caused by the formation of a greater number of hydrogen bonds by the

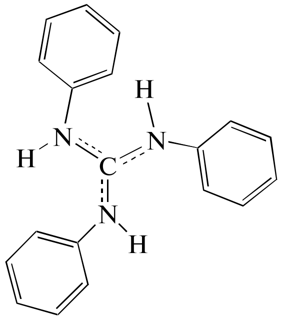
Table 2. Selected interatomic distances and bond angles in structure **I**

Bond	*d*, Å	Bond	*d*, Å
C(1)–N(1)	1.328(7)	Re(1)–O(2)	1.698(5)
C(1)–N(2)	1.328(7)	Re(1)–O(3)	1.699(5)
C(1)–N(3)	1.327(7)	Re(1)–O(4)	1.711(5)
C(2)–N(4)	1.346(7)	Re(2)–O(5)	1.696(5)
C(2)–N(5)	1.326(7)	Re(2)–O(6)	1.705(4)
C(2)–N(6)	1.351(7)	Re(2)–O(7)	1.723(5)
Re(1)–O(1)	1.668(5)	Re(2)–O(8)	1.688(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
C(1)N(1)C(3)	123.7(5)	O(1)Re(1)O(4)	111.2(3)
C(1)N(2)C(9)	127.2(5)	O(2)Re(1)O(4)	109.2(3)
C(1)N(3)C(15)	126.0(5)	O(3)Re(1)O(4)	110.1(3)
C(2)N(4)C(21)	125.1(5)	O(8)Re(2)O(5)	107.0(3)
C(2)N(5)C(27)	126.8(5)	O(8)Re(2)O(6)	109.6(3)
C(2)N(6)C(33)	124.2(5)	O(5)Re(2)O(6)	109.6(3)
O(1)Re(1)O(2)	107.5(3)	O(8)Re(2)O(7)	111.3(3)
O(1)Re(1)O(3)	108.6(3)	O(5)Re(2)O(7)	109.8(2)
O(2)Re(1)O(3)	110.3(3)	O(5)Re(2)O(7)	109.6(2)

triphenylguanidinium cation with the C(2) central atom (Table 3).

The conformational position of the phenyl rings is of special interest. The positions of phenyl rings correspond to the low-symmetry conformation (A) in all structures [9–18] containing the triphenylguanidinium cation found in the CCDC (version 5.33, August 2012). In compound **I**, unlike the described compounds [9–18], the phenyl rings in the triphenylguanidinium cation occupy the positions corresponding to the high-symmetry (C_{3h}) conformation (B), which was not observed earlier. This conformation is observed for both crystallographically independent cations.


(A)


(B)

The dihedral angles formed by the planes of the phenyl rings and CN_3 are 58.8(2)° (C(9)–C(14)), 62.1(2)° (C(3)–C(8)), 63.3(2)° (C(15)–C(20)) and 64.2(2)° (C(21)–C(26)), 53.5(2)° (C(27)–C(32)), 66.2(2)° (C(33)–C(38)), respectively. It is known from the literature data that in other structures (conformation A) these angles range from 32° to 71° [9–19]. Perhaps, the fairly narrow range of these angles in structure **I** (53.5°–66.2°) is related to the higher symmetry of conformation B.

The ReO_4^- anions are weakly distorted tetrahedra (Table 2). The average Re–O distance in structure **I** (1.699(5) Å) corresponds to the distances known from the literature for perrhenate ions at ambient temperature [20, 21].

The system of hydrogen bonds in structure **I** represents infinite branched chains in the [110] direction joining both independent formula units (Table 3, Fig. 1b). All hydrogen bonds are classified as simple [22]. In the triphenylguanidinium cation with the central C(2) atom, each of three NH groups form one hydrogen bond: two hydrogen bonds with the $Re(1)O_4^-$ anions and one hydrogen bond with $Re(2)O_4^-$. At the same time, in the triphenylguanidinium cation with the central C(1) atom, only one NH group forms a hydrogen bond with the $Re(1)O_4$ anion and another group forms a hydrogen bond with the water molecule. The oxygen atom in the latter molecule acts as a proton acceptor. In addition, the water molecule as a donor acceptor forms two more hydrogen bonds: one

Table 3. Geometric parameters of hydrogen bonds in structure **I**

Contact D–H···A	Distance, Å			Angle D–H···A, deg	Symmetry code for atom A
	D–H	H···A	D···A		
N(1)–H(1N)···O(9)	0.86	1.98	2.797(7)	159	–*x* + 1, –*y* + 1, –*z* + 1
N(2)–H(2N)···O(2)	0.86	2.05	2.872(7)	160	*x*, *y*, *z* + 1
N(6)–H(6N)···O(7)	0.86	2.12	2.896(7)	149	
N(5)–H(5N)···O(3)	0.86	2.01	2.828(7)	159	–*x* + 1, –*y*, –*z*
N(4)–H(4N)···O(1)	0.86	2.03	2.815(7)	151	
O(9)–H(39)···O(6)	0.848(19)	2.02(3)	2.849(6)	166(7)	*x* – 1, *y*, *z*
O(9)–H(40)···O(4)	0.837(19)	2.06(3)	2.838(7)	155(7)	*x* – 1, *y*, *z*

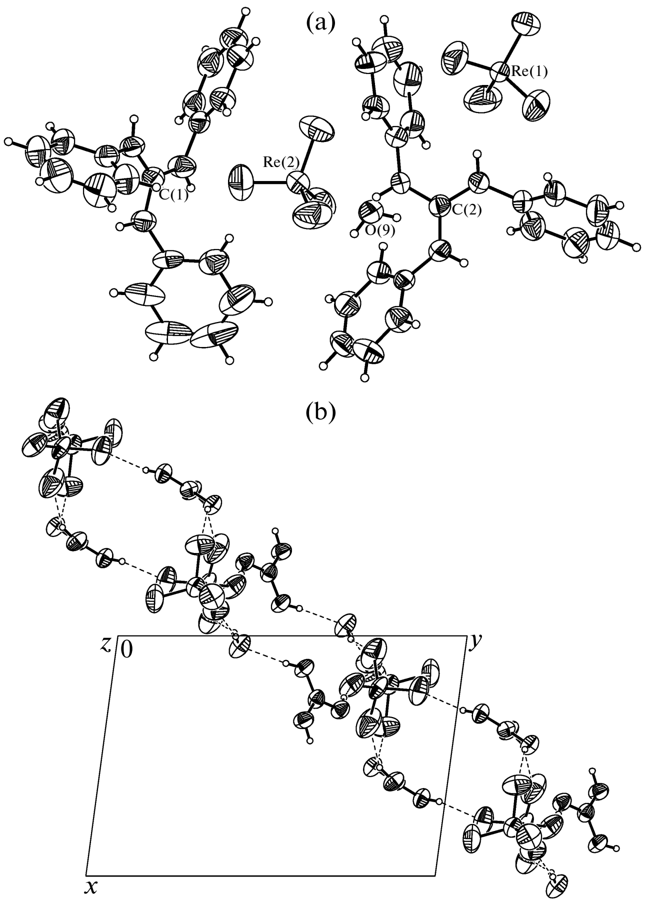


Fig. 1. (a) Molecular structure of compound **I** and (b) the system of hydrogen bonds in structure **I** (only CN_3 groups are shown for triphenylguanidinium cations).

hydrogen bond with each ReO_4^- anion. Thus, each NH group, except for N(3)H, and the oxygen atoms in the anions, except for O(5) and O(8), are included into one hydrogen bond.

The thermal studies of compound **I** were aimed at potential using of this compound for conversion to metallic rhenium. The DTA and TG methods detected the processes of dehydration, melting, and thermal decomposition (Fig. 2). At 373 K compound **I** begins to lose water. Anhydrous phase **Ia** begins to crystallize at the water loss about 30%, ceases at 413 ± 3 K, and is accompanied by the endothermic effect. According to the DTA data, the enthalpy of dehydration of compound **I** is $\Delta H_{\rm dehydr}^{(383\ \rm K)} = 10.0(8)$ kJ/mol. Compound **I** melts congruently at 441 ± 3 K. According to the DTA data, the enthalpy of melting for compound **Ia** is $\Delta H_{\rm m}^{(441\ \rm K)} = 16.6(9)$ kJ/mol.

Table 4. Indexing of the powder pattern of the second component of the composite phase, carbon-deficient rhenium carbide (Fig. 3c) ($a = 5.095$ Å), formed upon the thermolysis of a melt of triphenylguanidinium perrhenate under the conditions of insufficient blowing with an inert gas

No.	*hkl*	2θ (exp.)	2θ (calcd.)	Δ
1	2 0 2	50.70	50.604	0.096
2	3 1 1	60.30	60.153	0.147
3	4 0 0	74.26	74.374	−0.114
4	2 3 3	90.20	90.266	−0.66
5	4 0 4	117.60	117.542	0.070

Compound **Ia** begins to decompose at 458 ± 3 K. The process is endothermic, produces volatile organic fragments and solid X-ray amorphous products (Fig. 3), and ceases at 513 ± 3 K. Endothermicity of decomposition has been observed earlier for the whole series of perrhenates with tetraalkylammonium cations [23]. Note that, on the contrary, the thermal decomposition of the technetium analog, triphenylguanidinium pertechnetate, is exothermic [4]. Tetralalkylammonium pertechnetates and permanganates decompose also exothermally [24].

If thermolysis is carried out in argon at 450–520 K and then the sample is subjected to recrystallization annealing at the temperature not higher than 1250 K, the solid product is nanodispersed rhenium dispersed in the amorphous carbon matrix (Fig. 3a). The chemical analysis showed that the atomic ratio of rhenium to carbon in the solid phase can vary from 1 : 2 to 1 : 18, depending on the macrokinetic parameters of thermolysis (the temperature increase rate specified by a PRT-1200 temperature-programmed regulator and the rate of inert gas blowing). The carbon fraction in the products decreases with a decrease in the temperature increase rate and an increase in the blowing rate.

The sample with the certain ratio Re : C = 1 : 8 was subjected to recrystallization annealing at 1450 K. Three components were found in the solid-phase annealing product. The composition of the composite phase was determined by the X-ray diffraction data (Fig. 3c). The first component is metallic rhenium with the typical hexagonal close packed (hcp) structure. The second component has the cubic structure with $a = 5.095$ Å and $V = 132.48$ Å^3 (Table 4). The systematic quenchings in the X-ray diffraction pattern of the powder agree with the space group *Pm*3*m*. These characteristics are similar to the parameters of cubic phases of some lanthanide carbides (Ho_3C, Yb_3C, Sm_3C) and Fe_4N [25]. Probably, this phase represents carbon-deficient rhenium carbide isostructural to the described phases, whose formation has earlier been considered impossible. According to the chemical and X-ray diffraction analyses data, the third component is excessive amorphous or partially graphitized carbon formed by the carbonization of the starting triphenylguanidinium organic cation.

It seems probable that thermolysis provides favorable conditions for the reaction of a portion of highly dispersed rhenium, which is formed from triphenylguanidinium perrhenate, with highly dispersed car-

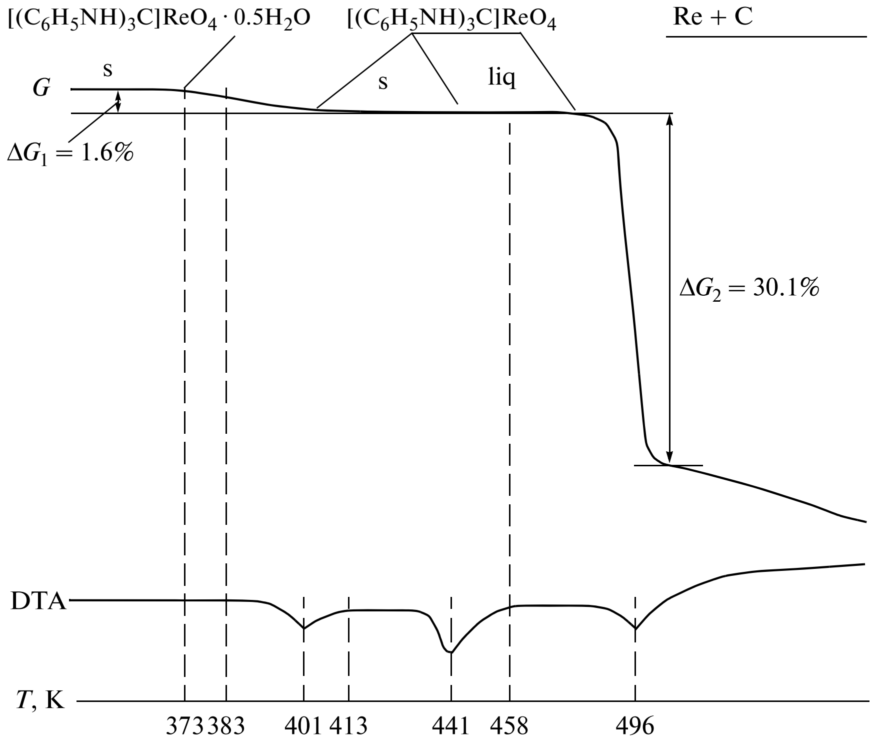


Fig. 2. Derivatothermogram of the dehydration, melting, and decomposition of triphenylguanidinium perrhenate hemihydrate.

bon, which is the carbonization product of the organic cation.

The study of the laser evaporation of this sample indirectly confirms the affinity of rhenium to carbon and, hence, the possibility of carbide formation. The stability of the obtained sample containing ~20% metallic rhenium and ~80% rhenium carbide in the course of laser evaporation was examined. The obtained mass spectrum is shown in Fig. 4. The formation of satellite isotopically split (185 and 187 au) doublets with an increment of 12 au attributed to the presence of Re$^+$, ReC$^+$, ReC$_2^+$, ReC$_3^+$, and ReC$_4^+$ ions was observed.

Initial sample **I** was also directly subjected to laser evaporation. In this case, numerous peaks assigned to the formation of organic ions (destruction products of the triphenylguanidinium cation) were in the spectrum among the peaks with the mass less than 170 au. However, only doublet (at 185–187 au) was observed among the peaks with the mass more than 170 au.

The formation of satellite doublets with an increment of 12 au in the course of the laser evaporation of rhenium carbide evidently indicates that the phase formed is stable under these conditions.

If the thermal decomposition of compound **Ia** at 450–520 K is carried out in an atmosphere of the reducing gas (hydrogen), the resulting solid product represents almost purely metallic rhenium. The isothermal recrystallization annealing at 1250 K of the

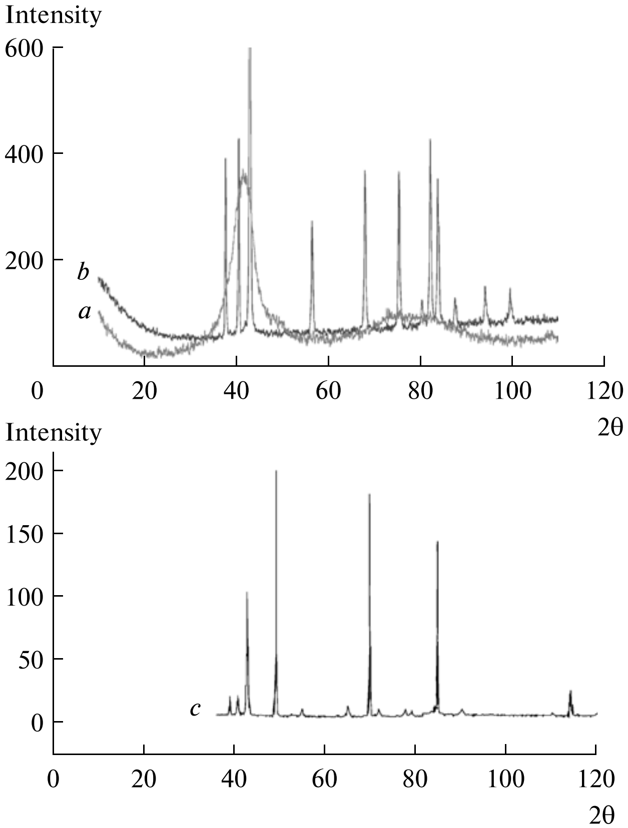


Fig. 3. X-ray diffraction patterns of powders of the solid decomposition products of triphenylguanidinium perrhenate (*a*) in argon at $T = 1250$ K, (*b*) in hydrogen at $T = 1450$ K, and (*c*) in argon at $T = 1450$ K.

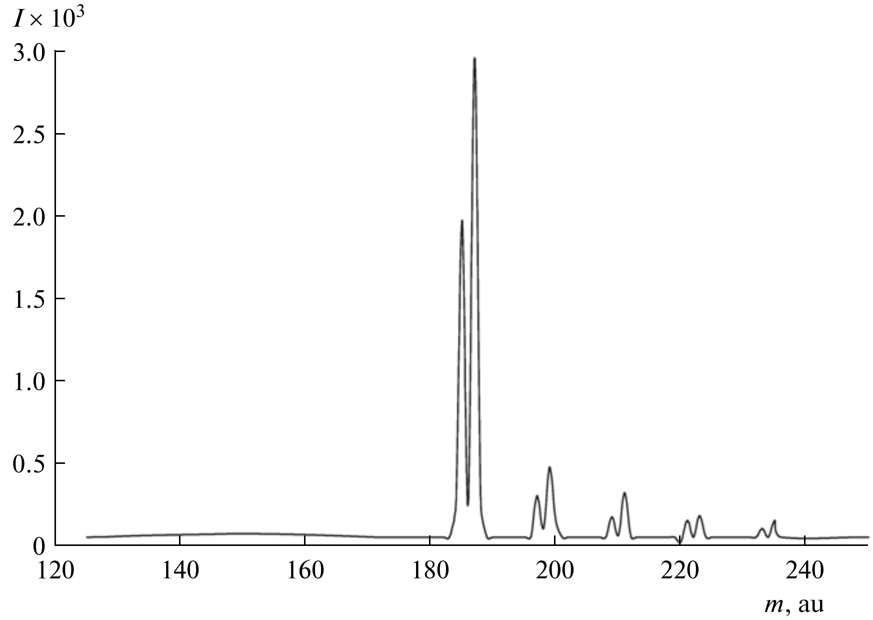


Fig. 4. Mass spectrum obtained upon the laser ionization in a LAMMA-1000 mass spectrometer of the sample, the product of thermolysis of compound **I** at 623 K and annealing (1373 K) in argon.

latter gives the hcp structure with the parameters $a = 2.7621(5)$, $c = 4.4575(5)$ Å, and space group $P6_3/mmc$ (Fig. 3b).

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