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Crystal Structure and Properties of $[Co(NH_3)_6][PdCl_4]Cl$

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Abstract—Complexes $[Co(NH_3)_6][PdCl_4]Cl$ (**I**) and $[Co(NH_3)_6]_2[PtCl_4]_3$ (**II**) are synthesized and characterized. Complex **I** is isolated for the first time. The compositions and structures of the complexes are confirmed by X-ray structure analysis (CIF file CCDC no. 1830657), X-ray diffraction analysis, IR spectroscopy, and elemental analysis. The thermal decomposition of complex **I** in air gives the three-phase product: Pd (space group $Fm3m$), PdO (space group $P\bar{4}n2$), and Co_3O_4 (space group $Fd3m$). The two-phase product consisting of metallic platinum Pt (space group $Fm3m$) and cobalt oxide Co_3O_4 ($Fd3m$) is formed as a result of the thermal decomposition of complex **II** is revealed that the single-phase product (a solid solution based on the noble metal and cobalt) can be obtained by the thermal decomposition of the corresponding binary complexes in a hydrogen flow or by chemical reduction using a solution of $N_2H_4 \cdot HCl$.

Keywords: complex formation, binary complexes, palladium, platinum, cobalt, bimetallic powders, thermal stability, chemical reduction

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INTRODUCTION

Heteronuclear binary complexes containing various metals as central atoms in the cationic and anionic moieties are interesting both from the viewpoint of extending scientific foundations of coordination chemistry and as precursors of powder polymetallic materials. The presence of different metals in the compound itself favors the formation of single-phase polymetallic powders upon the thermal or chemical decomposition of the heteronuclear binary complexes [1–5]. These single-phase polymetallic powders exhibit a high catalytic activity in diverse processes often exceeding the catalytic ability of monometallic powders of noble metals [6–8].

To the present time, a significant number of works is devoted to the study of the interaction of solutions containing the ammonia complexes $[M(NH_3)_5X]^{2+}$ (M = Co(III), Cr(III), Rh(III), Ir(III), and Ru(III); X is acido ligand) and the chloro complexes of platinum metals with the charge of the anionic moiety 2– [9, 10] leading, as a rule, to the formation of heteronuclear binary complexes with the molar ratio of metals equal to 1 : 1. It should be mentioned that heteronuclear binary complexes are often formed due to mixing solutions containing the initial metal complexes, and this procedure is not conjugated with experimental difficulties.

The reactions of the platinum(II, IV) and palladium(II) chloro complexes with the hexaamminocobalt(III) cation $[Co(NH_3)_6]^{3+}$ are studied to a considerably lower extent. The reactions of the luteo salt $[Co(NH_3)_6]Cl_3$ with solutions containing platinum metals were first mentioned in the second half of the 19th century [11, 12]. For example, W. Gibbs [11] showed that the iridium, platinum, rhodium, and palladium chloro complexes formed, under these conditions, precipitates of binary compounds. However, the compositions and properties of the formed compounds were not studied in detail. We have shown earlier [13] and confirmed later [14] the isolation of the $[Co(NH_3)_6]_2[PtCl_4]_3$ complex to the solid phase upon the reaction of $[Co(NH_3)_6]^{3+}$ with a solution containing tetrachloroplatinate(II) ions.

The purpose of this work is to synthesize a binary complex based on the $[Co(NH_3)_6]^{3+}$ cation and $[PdCl_4]^{2-}$ anion and to compare the composition and properties of this compound with those of the $[Co(NH_3)_6]_2[PtCl_4]_3$ complex synthesized under similar conditions.

EXPERIMENTAL

The following reagents were used: $CoCl_2 \cdot 6H_2O$ (reagent grade), $K_2[PtCl_6]$ (high-purity grade), and $PdCl_2$ (high-purity grade, Aurat). The reagents NH_4Cl, $N_2H_4 \cdot HCl$, and NH_3 and inorganic acids were reagent grade. The initial complexes $K_2[PtCl_4]$, $K_2[PdCl_4]$, and $[Co(NH_3)_6]Cl_3$ were synthesized using described procedures [15, 16].

Complexes $[Co(NH_3)_6]_2[PtCl_4]_3$ and $[Co(NH_3)_6][PdCl_4]Cl$ were prepared by mixing hydrochloric solutions (pH 2) containing the initial complexes of platinum metals(II), $[MCl_4]^{2-}$ (M = Pd(II), Pt(II)), and $[Co(NH_3)_6]^{3+}$ ($c^{in}_{Pd,Pt,Co}$ = 0.01 mol/L) at room temperature. The precipitates formed in ~1 h were filtered off, washed with alcohol, and dried at 30–40°C in air.

Hexaamminocobalt(III) tetrachloropalladate(II) $[Co(NH_3)_6][PdCl_4]Cl$ (**I**) was isolated as fine vinous plates. The yield of the product was 70.9%.

For $H_{18}N_6Cl_5CoPd$ (*FW* = 444.78)

Anal. calcd., %	H, 4.05	N, 18.9	Cl, 39.9	Co, 13.3	Pd, 23.9
Found, %	H, 3.9	N, 17.9	Cl, 40.3	Co, 12.5	Pd, 24.6

A single crystal of compound **I** was grown using the following procedure. A solution of $[Co(NH_3)_6]Cl_3$ (2 mL) in 0.01 M HCl ($c^{in}_{Pd,Co}$ = 0.01 mol/L) was slowly poured to a solution of $K_2[PdCl_4]$ (3 mL) in 0.01 M HCl. The starting molar ratio Pd : Co was 1.5 : 1. In a week, the crystals were separated from the mother liquor, washed with water, and dried in a desiccator to a constant weight.

Complex $[Co(NH_3)_6]_2[PtCl_4]_3$ (**II**) was an orange crystalline precipitate. The yield of the product was 71.6%.

For $H_{36}N_{12}Cl_{12}Co_2Pt_3$

Anal. calcd., %	H, 2.70	N, 12.6	Cl, 31.9	Co, 8.84	Pt 43.9
Found, %	H, 2.50	N, 12.9	Cl, 32.0	Co, 8.58	Pt 43.9

The isolated compounds are poorly soluble in water and 0.1–2 M HCl, insoluble in methanol, ethanol, ether, chloroform, toluene, methylene, heptane, and carbon tetrachloride, and soluble in 2–3 M solutions of HCl on heating.

Mother liquors and solutions obtained by the dissolution of weighed samples of the isolated compounds were analyzed to the content of platinum metals using the known spectrophotometric procedures with tin dichloride [17]. Analyses to cobalt were conducted by the complexonometric method [18].

Electronic absorption spectra of hydrochloric solutions were recorded on a SPECORD UV-Visible Helios spectrophotometer in a wavelength range of 200–1000 nm in quartz cells with an absorbing layer thickness of 1 cm. IR absorption spectra were recorded on an Equinox 55 FT-IR spectrometer (Bruker) in a frequency range of 200–4000 cm^{-1}. Differential thermal analysis was carried out in air on a Q-1500 D derivatograph (Paulik–Paulik–Erdey system, MOM, Hungary) with the simultaneous detection of four curves: differential (DTA), temperature (T), differential thermogravimetric (DTG), and integral mass changing curve (TG) using the firmware developed at the OOO IP Tetran in the LabVIEW 8.21 medium (National Instruments. Austin, Texas, USA). The temperature was measured using a platinum/platinum–rhodium (PP-1) thermocouple with an inaccuracy of ±5°C in the temperature range from 20 to 1000°C at a heating rate of 10 deg/min using α-Al_2O_3 as a standard. The weighed sample was 50–100 mg (weighing inaccuracy ±0.4 mg). The complexes were decomposed in a hydrogen flow in a tubular furnace in quartz boats at T = 500–550°C for 2 h.

The picnometric densities of $[Co(NH_3)_6][PdCl_4]Cl$ and $[Co(NH_3)_6]_2[PtCl_4]_3$ were determined using a U10 ultrathermostat according to a known procedure [19] at 20°C (**I**) and 22°C (**II**). The pinometric density (ρ_p) was calculated by the equation $\rho_p = (m_2 - m_0)\rho_{liq}/[(m_1 - m_0) - (m_3 - m_2)]$, where m_0 is the weight of the empty picnometer (g), m_1 is the weight of the picnometer with CCl_4 (g), m_2 is the weight of the picnometer with the powder sample (g), m_3 is the weight of the picnometer with the powder sample and CCl_4 (g), and ρ_{liq} is the density of CCl_4 (1.594 g/cm^3 at 20°C and 1.590 g/cm^3 at 22°C).

Metal powders were obtained from solutions as follows. Weighed samples (0.1 ± 0.001 g) of complexes $[Co(NH_3)_6][PdCl_4]Cl$ or $[Co(NH_3)_6]_2[PtCl_4]_3$ were dissolved in 3 M HCl (50 mL). The pH value was brought with an alkali solution to pH 11–12 using test-paper, a droplet of a solution of $N_2H_4 \cdot HCl$ with a concentration of 1 mol/L was added, and a fine black powder was immediately formed. The complexes were also decomposed by the treatment of a weighed sample of the substance with a 1 M solution of NaOH and the addition of a solution of $N_2H_4 \cdot HCl$ in a concentration of 1 mol/L to the pulp with stirring. A black powder was formed immediately. The powders were decanted from the mother liquors, multiply washed with water, and dried at 40°C to a constant weight.

The X-ray diffraction analyses (XRD) of the obtained heteronuclear binary complexes and their thermolysis products were carried out on DRON-3 (graphite monochromator), Bruker D8 (Ni filter), and HZG-4 (Ni filter) diffractometers using CuK_α radiation and rotation of the sample in the permanent (1 deg/min) and b-increment (increment 0.02°, exposure 10 s) regimes in a 2θ angle range of 20°–100°. Qualitative XRD was carried out by comparing

the X-ray diffraction data of the synthesized samples and phases belonging to this system and the isostructural samples and phases using the ICDD PDF-2 powder diffraction file database.

X-ray structure analysis was carried out on an Enraf-Nonius CAD4 automated diffractometer at room temperature (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The crystals of complex **I** ($FW = 444.78$) are tetragonal, space group $P4_22_12$, $a = 15.490(2)$, $c = 11.307(3)$ Å, $V = 2713.0(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.178$ g/cm^3, μ(MoK_α) = 3.506 mm^{-1}, and $F(000) = 1744$. Intensities of 13350 reflections (of them 2661 were independent reflections, $R_{int} = 0.0376$) were measured using the ω scan mode in the range $2.23° < \theta < 25.96°$ ($-19 \le h \le 3$, $-19 \le k \le 19$, $-13 \le l \le 13$). Experimental data were corrected taking into account the Lorentz and polarization factors [20]. An absorption correction was applied on the basis of measurements of equivalent reflection intensities (XPREP program in the SHELXTL package [21]). The structure was solved by a direct method and refined by full-matrix anisotropic least squares for F^2 for all non-hydrogen atoms (SHELXTL). All hydrogen atoms were placed in the calculated positions and refined by the riding model taking into account rotation about the Co–N bonds. The final values were $R_1 = 0.0238$ and $wR_2 = 0.0530$ for 2183 reflections with $I > 2\sigma(I)$ and 126 refinement parameters (GOOF = 1.086; $\Delta\rho_{max}$, $\Delta\rho_{min} = 0.438$, -0.558 e/Å^3). The absolute structure parameter was 0.13(4). The X-ray structure analysis was conducted at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences).

The crystallographic data for the structure of complex **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1830657; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The particle size was determined on a Delsa Nano analyzer (Beckman Coulter, Germany).

RESULTS AND DISCUSSION

The formation of heteropolynuclear binary complexes with the molar ratio of metals different from 1 : 1 is expected for the reactions of the studied heterocharge complex ions Co(III) and Pd(II) or Pt(II) (complex cation has the charge +3, and –2 is the anion charge). However, we revealed that the interaction of a solution containing $[Co(NH_3)_6]^{3+}$ cations with solutions containing the platinum metal chloro complexes $[MCl_4]^{2-}$ (M = Pd(II) or Pt(II)) afforded binary complexes differed in both the nature of the platinum metal and structure. If potassium tetrachloroplatinate(II) acts as the initial compound, complex **II** crystallizes with the molar ratio of the metals Co : Pt = 1 : 1.5 regardless of the specified initial molar ratio

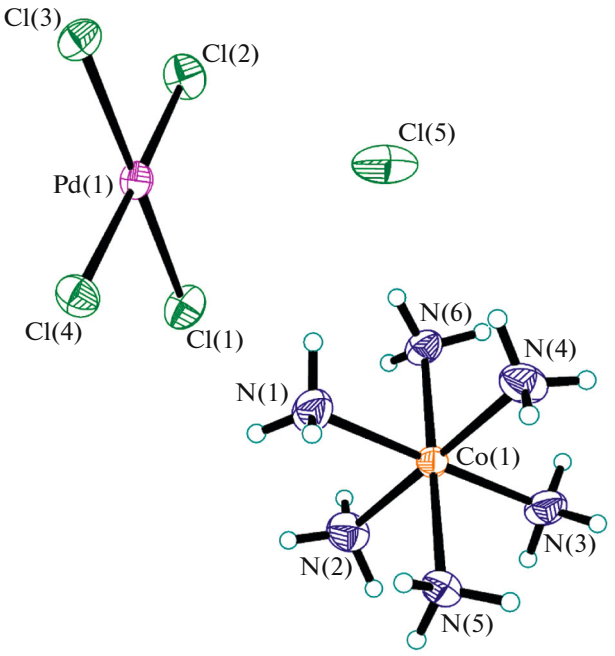

Fig. 1. Independent part in the structure of complex $[Co(NH_3)_6][PdCl_4]Cl$.

of metal ions in the mixed solutions (Co : Pt = 1 : (0.5–2.5)). If potassium tetrachloropalladate(II) is used as the initial complex, compound **I** ($[Co(NH_3)_6][PdCl_4]Cl$) is formed in which the molar ratio of the metals Co : Pd = 1 : 1 is also independent of the initial ratio of the Co(III) and Pd(II) metal ions in the mixed solutions. Complex **I** was isolated for the first time.

The structure of complex **I** consists of the octahedral $[Co(NH_3)_6]^{3+}$ cation, square $[PdCl_4]^{2-}$ anion, and chloride anion (Fig. 1). All structural units are arranged in the general positions. The cation is an almost regular octahedron with the *cis*-NCoN angles ranging from 87.71(15)° to 91.64(15)° and Co–N bond lengths of 1.960(3)–1.969(3) Å. The $[PdCl_4]^{2-}$ anion is an almost regular square with *cis*-ClPdCl angles of 89.23(6)°–91.30(4)° and Pd–Cl distances of 2.3051(12)–2.3115(13) Å. According to the CCDC data [22], the Co–N and Pd–Cl bond lengths in complex **I** have usual values for the complex ions $[Co(NH_3)_6]^{3+}$ and $[PdCl_4]^{2-}$.

All 18 hydrogen atoms of the amino groups are involved in the hydrogen bonds N–H···Cl with both all chlorine atoms of the $[PdCl_4]^{2-}$ ion and chloride anion. Five of these hydrogen bonds are bifurcate of the Cl···H(N)···Cl type. The N···Cl distances are 3.253(3)–3.650(3) Å, and the N–H···Cl angles vary from 111° to 173°. Numerous hydrogen bonds lead to the formation of a complicated 3D-bound supramolecular motif in the crystal.

The picnometric densities of complexes **I** (2.19 ± 0.02 g/cm^3) and **II** (2.94 ± 0.02 g/cm^3) are consistent

Table 1. Positions of the absorption bands in the IR spectra of the $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6][PdCl_4]Cl$, and $[Co(NH_3)_6]_2[PtCl_4]_3$ complexes and their assignment

Assignment	$[Co(NH_3)_6]Cl_3$ [23]	$[Co(NH_3)_6][PdCl_4]Cl$	$[Co(NH_3)_6]_2[PtCl_4]_3$
$\nu_{as}(NH_3)$	3240	3272, 3251 br.s	3273 br.s
$\nu_s(NH_3)$	3160	3150, 3118 br.s	3181 br.s
$\delta_{as}(HNH)$	1619	1606 s	1610 br.s
$\delta_s(HNH)$	1329	1330 vs	1341, 1323 vs
$\rho_r(NH_3)$	831	849 br.s	828 vs
ν(Co–N)	498	497 w.br	493
	477	480 m.br	461
	449	433 m.br	432
δ(HNH)	331	333 s	325
ν(M–Cl) (M = Pd(II), Pt(II))		322 s	312

with the data on the calculation of the X-ray density: 2.178 g/cm^3 (**I**, 20°C) and 2.938 g/cm^3 (**II**, 22°C [14]).

The positions of the absorption bands in the IR spectra of complexes **I** and **II** and their assignment are presented in Table 1. The absorption bands corresponding to vibrations of the initial complex ions $[Co(NH_3)_6]^{3+}$ and $[MCl_4]^{2-}$ (M = Pd(II), Pt(II)) [23] are retained in the IR spectra of the compounds. However, the replacement of the chloride ion in $[Co(NH_3)_6]Cl_3$ by anionic complex platinum metal chlorides results in some changes in positions of the absorption bands of the bonds in the IR spectra of the synthesized complexes. The N–H bond vibrations turned out to be most sensitive to the replacement of the anionic environment. For example, the $\nu(NH_3)$ stretching vibrations of the N–H bond in the IR spectrum of complex **II** undergo the high-frequency shift (33 cm^{-1} for $\nu_{as}(NH_3)$ and 21 cm^{-1} for $\nu_s(NH_3)$) indicating the enhancement of the N–H bond in the internal sphere of the $[Co(NH_3)_6]^{3+}$ cation compared to that in $[Co(NH_3)_6]Cl_3$ due to the weakening of the hydrogen bond between the complex cation and anion. A different situation is observed for complex **I**: the $\nu(NH_3)$ bands are broadened and split into two components. This can be explained by different anionic environments of the $[Co(NH_3)_6]^{3+}$ cation in compound **I** consisting of chloride $[PdCl_4]^{2-}$ anions. The observed changes and splitting in positions of the absorption bands of the bending and rocking vibrations of the N–H bonds (1620–800 cm^{-1}) in the IR spectra of both complexes indicate some distortion of the symmetry of the $[Co(NH_3)_6]^{3+}$ octahedron upon the formation of the binary complexes.

A comparison of the XRD patterns of the obtained products **I** and **II** and the initial compounds shows that the reflection peaks of the latter are absent in the XRD patterns of complexes **I** and **II**. The experimental XRD pattern of compound **II** synthesized in this work and the XRD pattern calculated for the same compound on the basis of the published single-crystal data [14] are presented in Fig. 2.

The thermal stability of the isolated heteronuclear binary complexes and the phase composition of the decomposition products (decomposition was conducted in air) were studied. The thermogravimetric curve of compound **I** is shown as an example in Fig. 3.

Complex **I** decomposes in a series of poorly separable stages. The decomposition onset is 230°C. The break in the mass loss (TG) curve is observed at 270°C. The sample loses 7.9% of the initial weight, which can be related to the removal of the out-of-sphere chloride ion (theoretical mass loss 7.97%). This stage is accompanied by a strong narrow endoeffect with a maximum at 262°C. The main mass loss (38.5%) occurs in a temperature range of 27–397°C. Then the weight of the sample increases by 2.1% in the TG curve to 491°C, which is likely caused by metal oxidation processes. This is confirmed by the exoeffect with a maximum in the curve of the DTA derivative at 440°C. The sample weight remains almost unchanged and no thermal effects are observed in a temperature range of 65–900°C. The complete decomposition is observed at 935°C, and the weight decreases by 3.4% in a range of 900–935°C. The total mass loss is 58.5%. Three thermolysis products were revealed by XRD: metallic palladium Pd (space group $Fm3m$), traces of palladium oxide PdO (space group $P\bar{4}n2$), and cobalt oxide Co_3O_4 (space group $Fd3m$).

The thermal stability of complex **II** turned out to be lower than that of complex **I**. The decomposition of complex **II** starts already at 130°C and proceeds via a series of difficultly separable stages accompanied by weak endoeffects (maxima at 260 and 348°C). The decomposition process completes at 620°C. The final value of the mass loss corresponds to the decomposition of the complex to metallic platinum and cobalt oxide Co_3O_4 (the mass loss was 43.1%, the experimen-

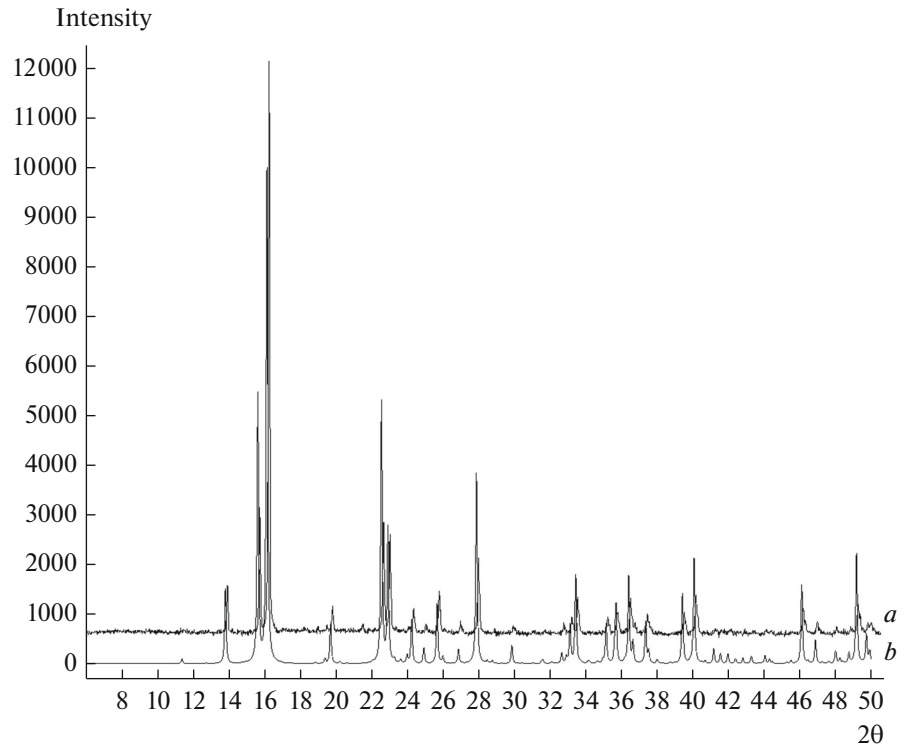

Fig. 2. (*a*) Experimental and (*b*) calculated from the single-crystal data XRD patterns of complex $[Co(NH_3)_6]_2[PtCl_4]_3$.

tal weight of the residue was 21.5 mg, and the calculated weight based on the sum of platinum and cobalt oxide was 21.2 mg). The XRD data for the thermolysis product confirmed the presence of two phases: metallic platinum Pt (space group *Fm*3*m*) and cobalt oxide Co_3O_4 (space group *Fd*3*m*). Thus, no single-phase products are formed upon the thermal decomposition of the complexes in air.

The study of the thermolysis products of complexes **I** and **II** in a hydrogen flow showed that solid solutions based on platinum metals were the thermal decomposition products in a reduction atmosphere. The XRD data for the products of the reduction of both complexes are presented in Table 2. The unit cell parameter $a = 3.748 \pm 0.005$ Å corresponding to a Pd–50 at % Co solid solution (the parameter presented in the ICDD PDF-2 65-6075 database is $a_{\alpha\text{-Co,Pd}} = 3.750$ Å (space group *Fm*3*m*)) was obtained for the product of the reduction of complex **I**. The bimetallic particles obtained by thermolysis in a hydrogen flow are characterized by an average particle diameter of 5.9 μm.

The unit cell parameter of the homogeneous phase in the sample obtained by the thermal decomposition of complex **II** in a hydrogen flow ($a = 3.799 \pm 0.004$ Å) corresponds to a solid solution based on platinum Pt_xCo_{1-x} (the parameter presented in the ICDD PDF-2 04-0802 database is $a_{Pt} = 3.923$ Å, and the unit cell parameter of intermetallic compound $CoPt_3$ is $a_{CoPt3} = 3.831$ Å [24]).

We revealed that the isolated compounds **I** and **II** are soluble in 2–3 M hydrochloric acid, which made it possible to characterize the state of the complex ions

Table 2. XRD data for the thermolysis products of complexes **I** and **II** in a hydrogen flow

Decomposition product				Pd (space group *Fm*3*m*) 89-4897		Pt (space group *Fm*3*m*) 04-0802	
I		**II**					
2θ	I_{rel}, %	2θ	I_{rel}, %	2θ	I_{rel}, %	2θ	I_{rel}, %
41.72	100	41.14	100	40.119	100	39.76	100
48.54	44	47.84	46	46.664	44	46.24	53
71.08	21	70.00	34	68.128	21	67.45	31
85.92	21	84.50	37	82.112	21	81.28	33

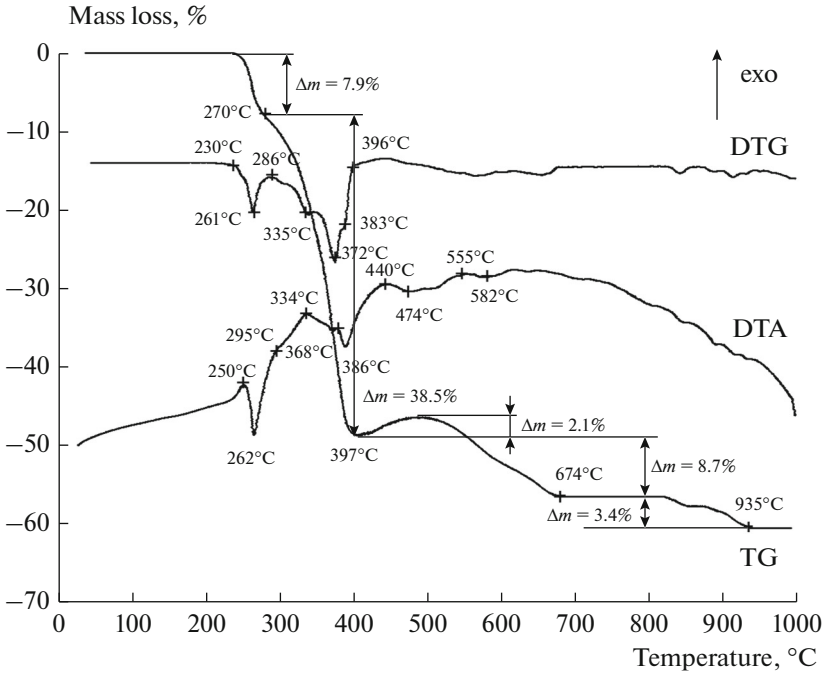

Fig. 3. Thermal decomposition curves for complex $[Co(NH_3)_6][PdCl_4]Cl$.

in solutions by electronic absorption spectroscopy. The electronic absorption spectra of individual solutions obtained by the dissolution of the precursors $K_2[PtCl_4]$ and $[Co(NH_3)_6]Cl_3$ in hydrochloric solutions and a solution obtained by the dissolution of a weighed sample (0.02 g) of compound **II** in 3 M HCl (25 mL of the solution) are presented in Fig. 4. The

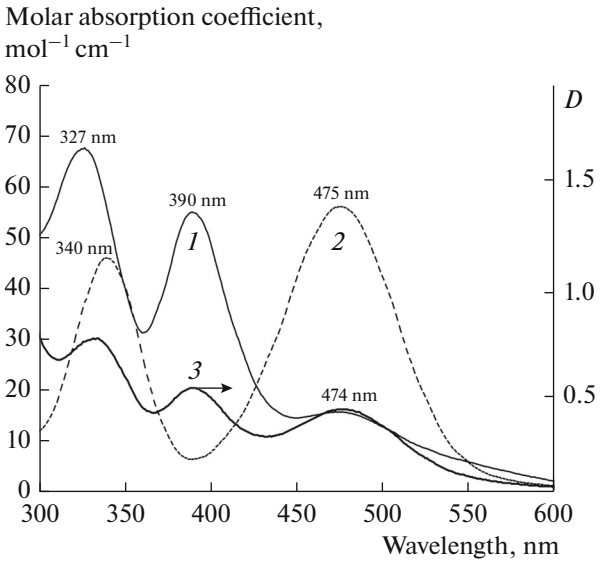

Fig. 4. Absorption spectra of solutions obtained by the dissolution of complexes (*1*) $K_2[PtCl_4]$ in 3 M HCl, (*2*) $[Co(NH_3)_6]Cl_3$ in 0.01 M HCl, and (*3*) $[Co(NH_3)_6]_2[PtCl_4]_3$ in 3 M HCl.

absorption spectrum of the solution obtained by the dissolution of the heteronuclear binary complex exhibits a broad absorption band at 333 nm with a shoulder at 327 nm. The absorption bands at 390 and 476 nm are the sum of the spectra of the initial complexes, as it is well seen from Fig. 4, and indicate that the complex spheres remain unchanged after the dissolution of the heteronuclear binary complexes. The absorption spectrum of the solution obtained by the dissolution of a weighed sample of complex **I** in 3 M HCl also represents the sum of the spectra corresponding to the absorption of the $[Co(NH_3)_6]^{3+}$ cation and $[PdCl_4]^{2-}$ anion.

We tested the possibility of preparing homogeneous bimetallic powders either by chemical reduction or from solutions containing dissolved heteronuclear binary complexes, or by reduction from the pulp consisting of complex **I** and a 1 M solution of NaOH. A solution of $N_2H_4 \cdot HCl$ served as a reducing agent.

Black precipitates were formed nearly immediately in all experiments. The extraction of the sum of metals to the solid product was higher than 99.9%.

The XRD patterns of the reduction products exhibit broadened reflections, which indirectly indicate in favor of the ultradispersed state of the particles. One phase corresponding to the solid solution Pd_xCo_{1-x} was revealed from the X-ray patterns of the product of the reduction of complex **I** from the solution. No oxide phases and metallic cobalt were found in the sample.

The bimetallic particles obtained by reduction from solutions are 2–3 μm in size. The preparation of nanosized powders requires additionally selected conditions.

To conclude, the $[Co(NH_3)_6][PdCl_4]Cl$ complex has been isolated and characterized for the first time. The thermal decomposition of the $[Co(NH_3)_6][PdCl_4]Cl$ and $[Co(NH_3)_6]_2[PtCl_4]_3$ complexes in air usually results in the formation of multiphase products containing metallic and oxide phases. The single-phase product, a solid solution based on the noble metal and cobalt, is formed due to thermal reduction in a hydrogen flow or chemical reduction using a solution of $N_2H_4 \cdot HCl$ as a reducing agent.

REFERENCES

1. Shubin, Yu.V. and Korenev S.V., Abstracts of Papers, *XX Mendeleevskii s"ezd po obshchei i prikladnoi khimii* (XX Mendeleev Congress on General and Applied Chemistry), Ekaterinburg, 2016, p. 130.
2. Asanova, T.I., Asanov, I.P., Zadesenets, A.V., et al., *J. Nanopart. Res.*, 2013, vol. 15, no. 10, p. 1994. doi 10.1007/s11051-013-1994-6
3. Pechenyuk, S.I., Semushina, Y.P., Mikhailova, N.L., and Ivanov, Y.V., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 3, p. 175. doi 10.1134/S1070328415020086
4. Zadesenets, A., Filatov, E., Plyusnin, P., et al., *Polyhedron*, 2011, vol. 30, no. 7, p. 1305. doi 10.1016/j.poly.2011.02.012
5. Martynova, S.A., Yusenko, K.V., Korol'kov, I.V., et al., *Russ. J. Coord. Chem.*, 2007, vol. 33, p. 530. doi 10.1134/S1070328407070093
6. Chen, Y., Mao, J., Shen, R., et al., *Nano Res.*, 2017, vol. 10, no. 3, p. 890. doi 10.1007/s12274-016-1344-y
7. Oleksenko, L.P. and Lutsenko, L.V., *Russ. J. Phys. Chem. A*, 2013, vol. 87, no. 2, p. 180.
8. Ellert, O.G., Tsodikov, M.V., Nikolaev, S.A., and Novotortsev, V.M., *Russ. Chem. Rev.*, 2014, vol. 83, no. 8, p. 718. doi 10.1070/RC2014v083n08ABEH004432
9. Pechenyuk, S.I. and Domonov, D.P., *J. Struct. Chem.*, 2011, vol. 52, no. 2, p. 412. doi 10.1134/S0036023610050128
10. Korenev, S.V., Venediktov, A.B., Shubin, Yu.V., et al., *J. Struct. Chem.*, 2003, vol. 44, no. 1, p. 46. doi 10.1023/A:1024980930337
11. Gibbs, W., *Am. J. Sci. Arts*, 1864, vol. 57, no. 109, p. 57. https://archive.org/details/mobot31753002152640/page/56.
12. Rogojski, J.B., *J. Prakt. Chem.*, 1852, vol. 56, p. 496.
13. Volchkova, E.V., Buslaeva, T.M., Lyutikova, E.K., et al., *Platinovye metally v sovremennoi industrii, vodorodnoi energetike i v sferakh zhizneobespecheniya budushchego "Berlin-PM 2010"* (Platinum Metals in Modern Industry, Hydrogen Power Engineering, and Life Provision Areas) (Proc. IV Int. Conf.) Berlin, 2010, p. 348.
14. Avisar-Levy, M., Levy, O., Ascarelli, O., et al., *J. Alloys Compd.*, 2015, vol. 635, p. 48. doi 10.1016/j.jallcom.2015.02.073
15. *Spravochnik. Sintez kompleksnykh soedinenii metallov platinovoi gruppy* (A Handbook. Synthesis of Complex Compounds of Platinum Group Metals), Chernyaev, I.I., Ed., Moscow: Nauka, 1972.
16. Klyuchnikov, N.G. *Rukovodstvo po neorganicheskomu sintezu* (Handbook on Inorganic Chemistry), Moscow: Khimiya, 1997.
17. Ginzburg, S.I. and Ezerskaya, N.A., *Analiticheskaya khimiya platinovykh metallov* (Analytical Chemistry of Platinum Metals), Moscow: Nauka, 1972.
18. *GOST 12560.1-78. Splavy palladii-serebryano-kobal'tovye. Metod opredeleniya kobal'ta i serebra* (Palladium–Silver-Cobalt Alloys. Method for Determination of Cobalt and Silver).
19. *ISO 8130-3:1992. Coating Powders*. Pt. 3: *Determination of Density by Liquid Displacement Pycnometer*. Geneva, 1992.
20. Harms, K., *XCAD4. Program for the Lp-Correction of Nonius CAD4 Data*, Marburg, 1997.
21. Sheldrick, G.M., *Acta Crystallogr., Sect. A*: *Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
22. Groom, C.R., Bruno, I.J., Lightfoot, M.P., and Ward, S.C., *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, vol. 2016, no. 72, p. 171.
23. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
24. *Spravochnik. Diagrammy sostoyaniya dvoinykh metallicheskikh sistem* (Handbook. Phase Diagrams of Binary Metallic Systems), Lyakishev, N.P., Ed., 1997, vol. 2.

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