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Powder X-ray diffraction study of the double complexes $[M(NH_3)_5Cl][M'Cl_4]$ as precursors of metal powders (M = Ir, Rh, Co; M′ = Pt, Pd)

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According to the results of powder X-ray diffraction study of the complex salts of composition $[M(NH_3)_5Cl][M'Cl_4]$ (M = Ir, Rh, or Co and M′ = Pt or Pd), the anhydrous salts crystallize in the orthorhombic system (space group *Pnma*) and are isostructural to the $[Ir(NH_3)_5Cl][PtCl_4]$ complex studied previously. The unit cell parameters of the resulting salts were refined. The metal powders, which were obtained by thermal decomposition of these salts under an atmosphere of hydrogen, were studied by powder X-ray analysis.

Key salts: iridium, rhodium, cobalt, platinum, palladium, chloropentammines, chloro complexes, powder X-ray diffraction analysis.

The present work was undertaken as part of our continuing studies on the double complex compounds, which are promising precursors of bi- and polymetallic powders. Compounds of the $[M(NH_3)_5Cl][M'Cl_4]$ series have been studied in sufficient detail. The crystal structure and selected properties of $[Ir(NH_3)_5Cl][PtCl_4]$ have been investigated.[1,2] Reduction of the latter complex afforded a metal powder, which was proposed to use for the preparation of a catalyst. The $[Co(NH_3)_5Cl][PdCl_4]$ complex was also synthesized and studied.[3] Previously,[4,5] we have prepared and characterized the complexes $[Rh(NH_3)_5Cl][PtCl_4]$ and $[Rh(NH_3)_5Cl][PdCl_4] \cdot H_2O$. It was demonstrated that thermal decomposition of the latter compounds under an inert or reductive atmosphere gave rise to finely dispersed powders of solid solutions of two metals. However, the question of whether these salts are isostructural to each other remained open. If these salts are isostructural, one would expect the preparation of metal phases containing three or more components, the content of each component being strictly specified by the starting composition of the solid solution of the complex salts.

In the present study, we carried out powder X-ray diffraction analysis of complexes of the above-mentioned series and the products of their reduction with hydrogen.

Experimental

The starting complexes $[Co(NH_3)_5Cl]Cl_2$, K_2PtCl_4, and K_2PdCl_4 were synthesized according to standard procedures.[6,7] The salt $[Rh(NH_3)_5Cl]Cl_2$ was prepared according to a procedure described by us previously.[4] A known procedure[7] for the synthesis of $[Ir(NH_3)_5Cl]Cl_2$ required prolonged heating in an autoclave, involved many steps, and was very laborious. In this procedure, numerous separation operations must be performed for obtaining pure samples. In addition, iridium chloride, which is characterized by a polynuclear structure[8] and is difficultly accessible, served as the starting compound. We developed a more convenient procedure for the synthesis of $[Ir(NH_3)_5Cl]Cl_2$. A small amount of water was added to a weighed sample of ammonium hexachloroiridate(IV) and the reaction mixture was treated with hydroxylamine hydrochloride with heating and stirring using a magnetic stirrer until the precipitate was completely dissolved and a dark-green solution was obtained. The reaction was accompanied by copious nitrogen liberation and was completed in several minutes. The resulting solution was cooled to ~20 °C and then solid NH_4Cl and NH_4HCO_3 and a concentrated solution of NH_4OH were added successively (24—27 moles of each reagent per mole of the iridium salt). The reaction mixture (pH ~9) was placed in a beaker, which was covered with a watch glass, and refluxed with weak heating for 6—10 h. As pH decreased, a 2—3 *M* solution of NH_4HCO_3 in NH_4OH (pH ~10) was added from two to three times. After the formation of a pale-yellow precipitate, the watch glass was removed and the mixture was heated until pH reached ~6. Then the solution was cooled and treated with hydrochloric acid until a ~10% HCl solution was obtained. The precipitate that formed was filtered off and successively washed with a ~1 *M* HCl solution, ethanol, and ether. To purify the compound, the precipitate was dissolved in a minimum amount of boiling H_2O, the hot solution was filtered through a paper filter, and an equal volume of concentrated HCl was added to the filtrate. Small pale crystals that rapidly precipitated were filtered off and washed as described above and then dried. The yield of pure $[Ir(NH_3)_5Cl]Cl_2$

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Table 1. Elemental analysis data for the complexes synthesized

Complex	Found/Calculated (%)					
	Sum of metals	Ir	Pd	Rh	Co	Pt
$[Ir(NH_3)_5Cl][PdCl_4]$	53.3 53.23	34.0 34.26	19.4 18.97			
$[Rh(NH_3)_5Cl][PdCl_4]$	44.3 44.37		22.8 22.56	21.5 21.81		
$[Co(NH_3)_5Cl][PdCl_4]$	38.6 38.67		24.6 24.88		13.3 13.78	
$[Co(NH_3)_5Cl][PtCl_4]$	49.2 49.19				11.1 11.41	38.1 38.78

was 70%. Calculated (%): Ir, 50.09; Cl, 27.72; ionic Cl, 18.48. Found (%): Ir, 50.0; Cl, 27.7; ionic Cl, 18.6. The electronic absorption spectrum of $[Ir(NH_3)_5Cl]Cl_2$ was identical with that published in the literature.[9]

Double complexes were precipitated at different temperatures by mixing 0.01 *M* solutions of the starting salts. The temperature of precipitation was thermostatically controlled with an accuracy of ±1 °C. The precipitates that formed were kept at a given temperature for 30 min, filtered off, successively washed with a minimum amount of H_2O and acetone, and dried in air. The compounds were characterized by elemental analysis and IR spectroscopy (Tables 1 and 2, respectively). Note that the salts of compositions $[Co(NH_3)_5Cl][PtCl_4]$ and $[Ir(NH_3)_5Cl][PdCl_4]$ were prepared for the first time.

Table 2. IR spectra of the complexes synthesized

Complex	ν(Co—N)	ρ(NH_3)	δ_s(NH_3)
	cm^{-1}		
$[Co(NH_3)_5Cl]Cl_2$	490	843	1308 (s)
$[Co(NH_3)_5Cl][PdCl_4]$	461	826 (s) 710 (w)	1297 (m) 1323 (s) 1369 (m)
$[Co(NH_3)_5Cl][PtCl_4]$	459	828 (s) 715 (w)	1302 (m) 1321 (s) 1368 (m)
$[Co(NH_3)_5Cl][PdCl_4] \cdot H_2O$	487	839 (s)	1306 (s)
$[Rh(NH_3)_5Cl]Cl_2$	457	812	1315 (s)
$[Rh(NH_3)_5Cl][PdCl_4]$	467	829 (s)	1294 (m) 1324 (s) 1359 (m)
$[Rh(NH_3)_5Cl][PtCl_4]$	467	833 (s) 710 (w)	1290 (m) 1320 (s) 1360 (m)
$[Rh(NH_3)_5Cl][PdCl_4] \cdot H_2O$	461	850 (s)	1316 (s)
$[Ir(NH_3)_5Cl]Cl_2$	475	860	1325 (s)
$[Ir(NH_3)_5Cl][PdCl_4]$	478	856 (s) 710 (w)	1325 (m) 1354 (s) 1386 (m)

The sums of the metals were determined by reducing the complexes under a stream of H_2 at 400 °C. The resulting metal powders were kept under a stream of helium at 600 °C for 15 min, cooled, and weighed. The metal powders thus obtained were studied by powder X-ray diffraction analysis. Separate analysis for the metals was carried out by atomic absorption spectroscopy on a Hitachi Z-8000 spectrometer with a Zeeman background correction. The interelement effects were eliminated by introducing $LaCl_3$ as the buffer additive. The IR spectra were recorded on a Bruker IFS-85 instrument.

Powder X-ray diffraction studies were carried out on a DRON-RM4 diffractometer (Cu-Kα radiation, graphite monochromator, reflection mode, scintillation detector with amplitude discrimination). The samples were prepared by coating an ethanolic suspension on to a polished side of a standard quartz cell. Polycrystalline silicon (a = 5.4309 Å) was used as the external standard. The X-ray diffraction patterns were measured in the step-by-step mode in the 2θ angle ranges of 5—55° and 5—135° for the complex salts and metal powders, respectively.

Results and Discussion

Most of the compounds synthesized did not form crystal hydrates whatever the temperature of precipitation was used. Previously,[4] it has been demonstrated that the complex salt $[Rh(NH_3)_5Cl][PdCl_4]$ crystallized at ~20 °C as a crystal hydrate with one water molecule per molecule of the salt. At 0 °C, the synthesis of this salt afforded the crystal hydrate of the same composition, whereas precipitation at 60 °C gave rise to the anhydrous product. An analogous situation was also observed in the case of the $[Co(NH_3)_5Cl][PdCl_4]$ complex with the only difference that the anhydrous salt crystallized at 50 °C. The presence or absence of H_2O molecules was confirmed by the IR spectroscopic data for the corresponding compounds and also by the weight loss upon calcination (140 °C) of the hydrated complexes. Depending on the temperature of precipitation, the water content in the solid compound

Table 3. X-ray diffraction characteristics of the complexes synthesized

Complex	a	b	c	V/Å^3	$d_{\text{X-ray}}$ /g cm^{-3}	Color
	Å					
$[Co(NH_3)_5Cl][PtCl_4]$	16.335(10)	8.015(5)	9.331(5)	2.808	1221.7(1.0)	Cherry
$[Co_{0.5}Rh_{0.5}(NH_3)_5Cl][PtCl_4]$	16.404	8.044	9.373	2.891	1236.8	Dark-red
$[Co_{0.9}Rh_{0.1}(NH_3)_5Cl][PtCl_4]$	16.334	8.019	9.329	2.828	1221.9	Cherry
$[Rh(NH_3)_5Cl][PtCl_4]$	16.496	8.086	9.423	2.961	1256.9	Red
$[Ir(NH_3)_5Cl][PtCl_4]$	16.518	8.108	9.428	3.417	1262.7	Red
$[Co(NH_3)_5Cl][PdCl_4]$	16.343	7.967	9.422	2.315	1226.7	Cherry
$[Rh(NH_3)_5Cl][PdCl_4]$	16.508	8.046	9.530	2.475	1265.8	Pale-brown
$[Ir(NH_3)_5Cl][PdCl_4]$	16.544	8.075	9.538	2.924	1274.2	Yellow-green

can vary. Attempts to prepare hydrated complexes of other compounds of this series failed and anhydrous salts crystallized even at 0 °C.

In the IR spectra of the anhydrous complexes (see Table 2), the $\delta_s(NH_3)$ bending vibration band is split. For example, the IR spectrum of $[Co(NH_3)_5Cl][PdCl_4]$ has three bands in this region (at 1297, 1323, and 1369 cm^{-1}), whereas the IR spectrum of $[Co(NH_3)_5Cl][PdCl_4] \cdot H_2O$ has only one band at 1306 cm^{-1}. The IR spectrum of the starting complex $[Co(NH_3)_5Cl]Cl_2$ also shows one $\delta_s(NH_3)$ band at 308 cm^{-1}.

The X-ray diffraction patterns of all anhydrous complexes were indexed within the orthorhombic system by analogy with the $[Ir(NH_3)_5Cl][PtCl_4]$ salt[2] whose structure has been established previously by single-crystal X-ray diffraction analysis. The unit cell parameters were refined by the least-squares method based on the positions of the well-resolved reflections in the 2θ angle range of 30—55° (Table 3). The good agreement of the experimental X-ray patterns with those calculated based on the structural data for $[Ir(NH_3)_5Cl][PtCl_4]$ (space group *Pnma*, $Z = 4$) taking into account the corresponding refined parameters confirms that the compounds under study are single-phase.

Earlier, the X-ray diffraction pattern of the $[Co(NH_3)_5Cl][PdCl_4]$ complex has been indexed within the hexagonal unit cell with a volume $V = 2662$ Å^3.[3] However, it is more likely that the complex of the same composition obtained by us is isostructural to the other members of the series and has the orthorhombic unit cell with a smaller volume ($V = 1227$ Å^3) (Fig. 1).

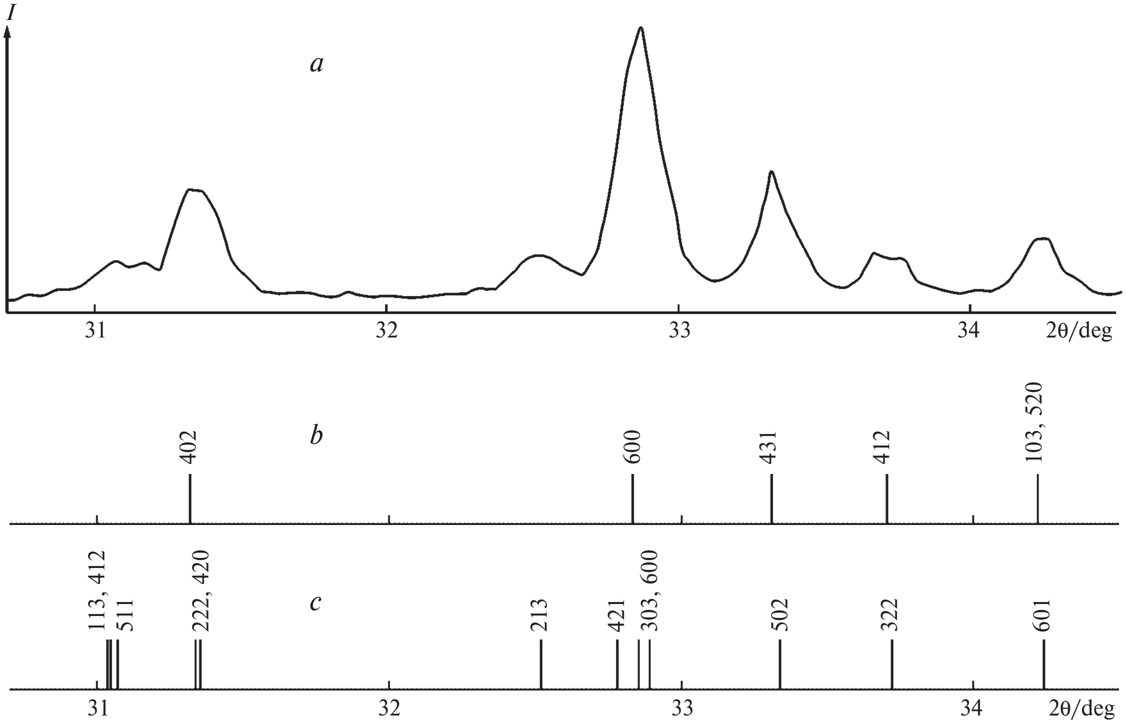

Fig. 1. Fragment of the experimental X-ray diffraction pattern for the complex salt $[Co(NH_3)_5Cl][PdCl_4]$ (*a*) and the positions and indices of the reflections calculated for the hexagonal (*b*) and (*c*) orthorhombic unit cells.

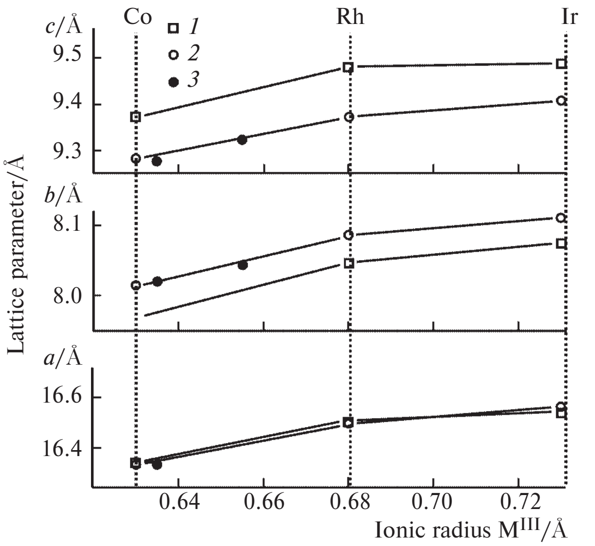

Fig. 2. Dependence of the unit cell parameters of the complex salts on their chemical compositions: *1*, complex salts with the $[PdCl_4]^{2-}$ anion; *2*, complex salts with the $[PtCl_4]^{2-}$ anion; *3*, solid solutions of the salts.

The relationship between the unit cell parameters of the complex salts and their chemical compositions is shown in Fig. 2. The replacement of the palladium atom in the $[M'Cl_4]^{2-}$ anion by the platinum atom has no effect on the *a* parameter (it remains unchanged to within 0.1%), whereas the *b* parameter increases by 0.5—0.8% and the *c* parameter decreases by 0.8—1.1%. To the contrary, all unit cell parameters increase as the size of the central atom in the cation ($[M(NH_3)_5Cl]^{2+}$) of the complex increases.

We failed to index the X-ray diffraction patterns of the crystal hydrates $[M(NH_3)_5Cl][M'Cl_4] \cdot H_2O$. The X-ray patterns of the hydrated salts with different elemental compositions are similar and were reproduced from synthesis to synthesis. It can be assumed that the hydrated complexes are also isostructural to each other.

Thermolyis of the resulting compounds under an atmosphere of hydrogen at 400 °C afforded homogeneous metal phases, which were substitution solid solutions with the face-centered cubic cells analogous to those of the starting metals. It is known[10] that each metal pair forms equiatomic solid solutions in alloys quenched from temperatures above 600 °C. However, data on the low-temperature regions of the phase diagrams are lacking because of the low rate of diffusion in alloys. Hence, no conclusions can be made of whether the solid solutions obtained by thermolysis reached the thermodynamical equilibrium. The X-ray diffraction characteristics of the metal powders are given in Table 4. The diffraction reflections are substantially broadened due to the small size of the crystallites. The sizes of the coherent scattering regions (CSR), which were calculated according to the approximate Scherer formula,[11] are given in Table 4.

Table 4. X-ray diffraction characteristics of the metal powders prepared by reducing the complexes under a stream of H_2 at 400 °C

Phase	a^a	Δ^b/Å	<CSR>^{c}	Phase content (%)
IrPd	3.858(1)	+0.007	70—85	100
RhPd	3.845	−0.002	50—80	100
CoPd	3.759^d	+0.042	150—290	96^d
IrPt	3.8852(8)^e	+0.008	100	—
RhPt	3.863	0.000	90	100
CoPt	$a = 2.684^f$ $c = 3.702^f$	—	—	100

[a] The parameter of the face-centered cubic lattice.
[b] The deviation from Vergard´s law.
[c] The average size of the coherent scattering region.
[d] The $Co_{52}Pd_{48}$ solid solution containing 4% of Pd.
[e] The $Ir_{45.3}Pt_{54.7}$ solid solution according to the published data.[1]
[f] The unit cell parameters of the CuAu-type tetragonal lattice.

Taking into account the stoichiometry of the starting complexes and the fact that the powders are single-phase, the resulting solid solutions have equiatomic compositions. Hence, if Vergard's rule is obeyed by the compounds, the unit cell parameters of each sample would be close to the average of the corresponding unit cell parameters of the components. For most of the samples, the calculated parameters deviate (Δ) only slightly from the above-mentioned values. It should be emphasized that the parameter of the face-centered cubic lattice of the equiatomic iridium—palladium solid solution, which was prepared by thermolysis of the $[Ir(NH_3)_5Cl][PdCl_4]$ salt, is equal to the corresponding parameter for the $Ir_{0.5}Pd_{0.5}$ solid solution, which has been prepared by us previously[12] from the $[Pd(NH_3)_4][IrCl_6]$ complex.

Thermal decomposition of the $[Co(NH_3)_5Cl][PtCl_4]$ salt under an atmosphere of H_2 afforded the CoPt intermetallide with the CuAu-type structure (the tetragonal system, the space group *P*4/*mmm*), which is stable below 825 °C.[10]

To examine the possibility of some cobalt atoms in the double cobalt—platinum complex being replaced by the rhodium atoms, we synthesized two samples of compositions $[Co(NH_3)_5Cl]_{0.5}[Rh(NH_3)_5Cl]_{0.5}[PtCl_4]$ (**1**) and $[Co(NH_3)_5Cl]_{0.9}[Rh(NH_3)_5Cl]_{0.1}[PtCl_4]$ (**2**). The samples were precipitated at ~20 °C by adding an excess of a solution of $K_2[PtCl_4]$ to a solution containing a mixture of Co and Rh pentammines in ratios of 1 : 1 and 9 : 1, respectively. The metal ratios in complexes **1** and **2**, which were determined by atomic absorption spectroscopy, were as follows: Co : Rh : Pt = 0.47 : 0.54 : 1.0 and 0.91 : 0.10 : 1.0, respectively. According to the powder X-ray diffraction data, the compounds are single-phase and isostructural to other salts of this series. The calculated unit cell parameters (see Table 3, Fig. 2) are indica-

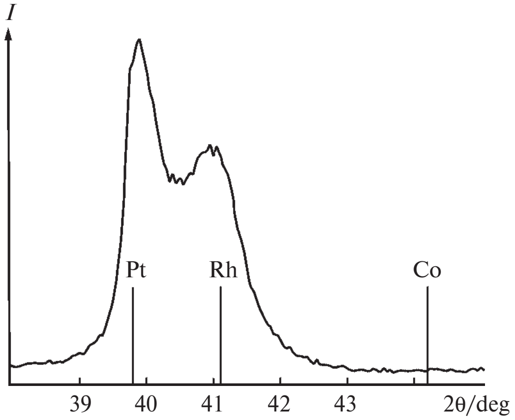

Fig. 3. Fragment of the X-ray diffraction pattern (the 111 reflection) for the metal powder obtained by thermolysis of the complex salt $[Co(NH_3)_5Cl]_{0.5}[Rh(NH_3)_5Cl]_{0.5}[PtCl_4]$. The positions of the corresponding reflections for pure metals are indicated by vertical bars.

tive of the formation of substitution solid solutions of the corresponding double complexes. Reduction of salt **1** with hydrogen gave rise to a mixture of two face-centered cubic phases with the unit cell parameters of 3.826 and 3.917 Å, respectively. The fragment of the X-ray diffraction pattern of this metal powder containing the (111) reflection is shown in Fig. 3. The observed unit cell parameters are attributable to the fact that decomposition of this complex gave rise to two three-component substitution solutions based on rhodium and platinum, respectively. In addition to the above-mentioned phases, thermolysis of salt **2** afforded a small amount of the CoPt intermetallide.

Hence, the fact that the complex salts of the series under consideration are isostructural to each other makes it possible to synthesize their substitution solid solutions of the desired composition $[M^1(NH_3)_5Cl]_x[M^2(NH_3)_5Cl]_{1-x}[M'Cl_4]$. The synthesis of the precursors with a specified ratio of the metals exhibiting complex-forming ability provides a way of preparing two- and three-component metal powders possessing new characteristics.

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