# SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Double Complex Salts $[Pt(NH_3)_5Cl][M(C_2O_4)_3] \cdot nH_2O$ (M = Fe, Co, Cr): Synthesis and Study

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**Abstract**—Double complexes  $[Pt(NH_3)_5Cl][Fe(C_2O_4)_3] \cdot 4H_2O$ ,  $[Pt(NH_3)_5Cl][Co(C_2O_4)_3] \cdot 2H_2O$ , and  $[Pt(NH_3)_5Cl][Cr(C_2O_4)_3] \cdot 4H_2O$  were synthesized and studied by single-crystal X-ray diffraction, X-ray phase analysis, differential thermal analysis, elemental analysis, and IR spectroscopy. The crystal structures of the compounds were examined from the viewpoint of the close packing of coordination polyhedra. The thermal properties of the synthesized complexes and  $K_3[M(C_2O_4)_3]$  salts (M = Fe, Co, Cr) were compared. A procedure for the synthesis of the FePt, CoPt, and CrPt intermetallic compounds through the thermolysis of the obtained complexes was developed.

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The synthesis of new double complex salts (DCS) using an ion containing a platinum-group metal and a counterion containing a base metal is of great interest for researchers, because these compounds can serve as precursors of various bimetallic materials. One example of using similar systems is the preparation of finely dispersed particles of solid solutions of metals or intermetallic compounds on various supports for the production of highly efficient catalysts [1] with a lowered content of noble metals.

Here, we describe the synthesis and properties of three new DCS:  $[Pt(NH_3)_5Cl][Fe(C_2O_4)_3] \cdot 4H_2O(I), [Pt(NH_3)_5Cl][Co(C_2O_4)_3] \cdot 2H_2O(II)$ , and  $[Pt(NH_3)_5Cl][Cr(C_2O_4)_3] \cdot 4H_2O(III)$ . In addition, we prepared the corresponding bimetallic powders and developed a procedure for the synthesis of the FePt, CoPt, and CrPt intermetallic compounds.

# **EXPERIMENTAL**

The initial  $[Pt(NH_3)_5Cl]Cl_3$ ,  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ ,  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ , and  $K_3[Cr(C_2O_4)_3]$  were synthesized according to described procedures [2, 3]. To increase the yield of  $[Pt(NH_3)_5Cl]Cl_3 \cdot H_2O$  (Tschugaeff's salt), excess hydrochloric acid was added to the mother solution obtained after the main portion of the salt was filtered, and the mixture was left for a week. As a result, an additional portion of the product was obtained as large needle-like crystals.

Synthesis of complex I. Equimolar amounts of  $[Pt(NH_3)_5Cl]Cl_3$  and  $K_3[Fe(C_2O_4)_3]$  were dissolved in minimum amounts of water in two beakers, and then a

solution of  $K_3[Fe(C_2O_4)_3]$  was poured with stirring to a solution of Tschugaeff's salt. A fine precipitate of the light green salt immediately appeared. After 1 h, the precipitate was filtered through a preliminarily weighed glass filter, washed with a minimum amount of ice-cold water and a minor amount of acetone, and dried in air. The yield was 90–97%.

**Syntheses of complexes II and III** were carried out similarly. In both cases, the yield was 90–95%. These complexes were green and blue colored, respectively.

The following method was used to obtain single crystals of the DCS. A U-shaped tube was half-filled with a hot 3% solution of agarose, and the solution was let to congeal. A solution of Tschugaeff's salt was poured into one column of the tube, and the other column was filled with a solution of the salt of the corresponding oxalate complex. The open ends of the tube were sealed, and the tube was left in the dark for 1 week. As a result of diffusion of the solution, transparent crystals of the DCS were formed as orthorhomic plates with a size to 0.1 mm in the middle of the tube.

The thermal properties of the compounds were studied on a Q-1000 derivatograph modified for operating under various gaseous atmospheres. A ~100-mg test sample was placed in a quartz crucible without a cover and heated with a rate of 7–10 K/min under helium flowing at a rate of 150 mL/min.

**X-ray diffraction analysis** of polycrystalline samples was carried out on a DRON-SEIFERT-RM4 diffractometer (Cu $K_{\alpha}$  radiation, graphite monochromator on reflected beam, scintillation detector with amplitude discrimination). Samples were prepared by spreading

Parameter	Ι	II	III	
FW	575.39	571.54	542.48	
Space group	Pccn	<i>P</i> 2 <sub>1</sub>	Pccn	
<i>a</i> , Å	39.0123(2)	8.5158(2)	38.901(2)	
b, Å	13.7232(7)	12.6409(4)	13.7267(7)	
<i>c</i> , Å	14.8990(8)	8.5726(3)	14.9141(8)	
β, deg	90	105.000(3)	90	
<i>V</i> , Å <sup>3</sup>	7976.5(4) 891.38(2		7963.9(7)	
$\rho_{calcd}$ , g/cm <sup>3</sup>	2.33	2.50	2.30	
Ζ	16	2	16	
$\theta$ range, deg	2.31-30.47	2.46-32.58	2.08-27.48	
Number of reflec- tions: total/inde- pendent	11093/6104	8310/5898	9118/5958	
Index range	-51 < h < 55,	-12 < h < 9,	-50 < h < 40,	
	-19 < k < 9,	-17 < k < 19,	-8 < k < 17,	
	-19 < l < 12	-12 < l < 10	-19 < <i>l</i> < 15	
Goodness-of-fit (for $F^2$ )	1.117	0.771	1.072	
$\Delta \rho_{max}, \Delta \rho_{min}, e \text{ Å}^{-3}$	2.545, -6.542	2.072, -0.993	2.037, -3.172	
Number of re- fined parameters	554	258	553	
$R_1$ and $wR_2$ for $I > 2\sigma(I)$	0.0509, 0.1093	0.0218, 0.0460	0.0511, 0.1184	
$R_1$ and $wR_2$ for all reflections	0.0817, 0.1589	0.0260, 0.0471	0.0896, 0.1326	

Table 1. Crystal data and experimental details for DCS

an alcohol suspension on the polished side of a fused quartz cell. A sample of polycrystalline silicon (a = 5.4309 Å) prepared similarly was used as an external standard. Diffraction patterns were detected in the step-to-step mode (for the complex salts, in the 2 $\theta$  range

from 5° to 60°; for thermolysis products, from 5° to  $135^{\circ}$ ).

The diffraction patterns of the prepared compounds were completely indexed using single-crystal data, which indicates that the samples were single phases identical to the single crystal. X-ray diffraction analysis of thermolysis products was carried out by analogy to the diffraction patterns of the pure metals and intermetallic compounds presented in the PDF file [4]. The parameters of the metal phases were refined for the whole data body using the PowderCell 2.3 applied program [5].

**X-ray structure analysis of compounds I–III** (the refinement of unit cell parameters and the measurement of diffraction refection intensities determining crystal structures) was carried out on a Bruker AXS P4 automated diffractometer (Mo $K_{\alpha}$  radiation, graphite monochromator,  $\theta/2\theta$  scan mode, room temperature). The crystallographic parameters and details of the experiment and structure refinement for complexes **I–III** are presented in Table 1. The structures were solved by the heavy atom method and refined in the anisotropic approximation. All calculations were performed using the SHELX97 program package [6].

The coordinates of atoms, bond angles, and interatomic distances are available from the authors.

#### **RESULTS AND DISCUSSION**

The crystals of complexes **I** and **III** are isostructural to each other and are not isostructural to the monoclinic crystals of complex **II**. The crystal structure of  $K_3[M(C_2O_4)_3] \cdot 3H_2O$  (M = Fe, Cr) differs from that of  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$  [7].

The unit cell of complex I is shown in Fig. 1. The FeO<sub>6</sub> octahedron around the complex anion is less distorted than that in the precursor  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ . The minimum and maximum "right" OFeO angles in the FeO<sub>6</sub> octahedra are 79.4° and 105.8° in the precursor salt and 80.4° and 96.4° in complex I. For the



Fig. 1. Unit cell of  $[Pt(NH_3)_5C1][Fe(C_2O_4)_3] \cdot 4H_2O$ . The oxygen atoms of the water molecules are shaded.



**Fig. 2.** Mutual arrangement of cationic and anionic layers in  $[Pt(NH_3)_5Cl][Fe(C_2O_4)_3] \cdot 4H_2O$  and  $[Pt(NH_3)_5Cl][CrOx_3] \cdot 4H_2O$  (positions of the Fe (Cr) atoms are gray, and those of the Pt atoms are white).

 $[Pt(NH_3)_5Cl]^{3+}$  complex cation, this distortion is noticeably weaker: the deviations of the angles from ideal values are within 1°. The metal–ligand distances also change insignificantly and fall within the experimental error.

Due to a comparatively low symmetry and large sizes of the complex ions, the structures of crystals I–III are rather loosen. Large channels 4.5–5.5 Å in diameter allow crystallization water molecules to incorporate into the structures.

In the crystals of complexes **I–III**, the complex cations and anions form separate layers at distances of 4.8–4.9 Å. In a crystal of complex **I** (Fig. 2), the distances are as follows: Pt…Fe 5.48–5.88Å, Fe…Fe 6.28–7.78 Å, and Pt…Pt 7.20–7.78 Å. In the structure of complex **II**, layers are also formed but they are built according to another principle. The Pt and Co atoms form common layers between which crystal-water molecules are arranged also as layers (Fig. 3).

The presence of crystal water is also confirmed by the IR spectra of the synthesized DCS (absorption bands at  $3600-3400 \text{ cm}^{-1}$ ).

All compounds synthesized were subjected to thermal decomposition in a hydrogen atmosphere for the following two purposes: carrying out the elemental analysis of the DCS to the sum of the metals formed upon decomposition and obtaining PtM (M = Fe, Co, Cr) intermetallic compounds. Thermolysis in a hydrogen atmosphere yields metal powders. Their phase composition depends on the heating conditions. A set of experimade it possible to optimize the thermolysis of the oxalate DCS to increase the yield of the intermetallic compounds. A weighed boat with the compound under study was placed in a quartz tubular reactor through which hydrogen was passed. The reactor was first heated to 400°C using a split tubular oven. The sample was stored at this temperature for 0.5 h, then the temperature was increased to 700°C, and the sample was stored for 2 h more. Then, the reactor was filled with helium, and the sample was stored for 0.5 h under these conditions. Then, the reactor with the boat was cooled to room temperature, and the boat with the product was weighed. The annealing in helium is necessary to prevent hydrogen absorption by metal products: the samples can ignite on contact with atmospheric oxygen. A characteristic feature of the decomposition in hydrogen of all the synthesized DCS is that the complexes change to black in the temperature interval from 100 to 150°C, and the change itself takes ~5 s and is well visualized. The data obtained are presented below.

ments on the decomposition of  $[Pt(NH_3)_5Cl][Fe(C_2O_4)_3]$ 

Complex	Found $\Sigma$ FW, wt $\%$	Calcd, wt %	
Ι	37.44	32.18	
II	37.65	37.64	
III	35.92	31.84	

This divergence between the experimental and calculated data is due to the fact that the DCS powders were taken for elemental analysis while the number of



**Fig. 3.** Mutual arrangement of cationic and anionic layers in the crystal of  $[Pt(NH_3)_5Cl][Co(C_2O_4)_3] \cdot 2H_2O$  (positions of the central Pt atoms are white, and those of Co are gray) between which layers of water molecules are arranged. The Pt…Co distances are 5.14–6.00 Å.

water molecules in the structure was determined for single crystals. Evidently, the evaporation of weakly bound water occurred more rapidly in the powders and, hence, the results were underestimated.

The final thermolysis products of compounds I and III are the corresponding intermetallic compounds. The diffraction pattern of the sample of complex II contains broadened low-intensity superstructural peaks. A solid solution with a low degree of ordering is formed, because CoPt begins to decompose at ~800°C [8]. The unit cell parameters of the metallic thermolysis products are given in Table 2.

The decomposition of the DCS in a hydrogen atmosphere at a constant rate without stopping at certain temperature yields polyphase systems containing phases of pure metals and their partially ordered solid solutions rather than intermetallic compounds. The

 Table 2. Phase compositions of the degradation products of DCS I–III in hydrogen

Com- plex	Composition of degradation product	<i>a</i> , Å	<i>c</i> , Å	CSR, Å
Ι	PtFe	3.860(2)	3.732(2)	200-300
II	Pt <sub>0.5</sub> Co <sub>0.5</sub>	3.760(5)	3.750(5)	250-350
III	PtCr	3.837(2)	3.825(5)	250-350

metal powder obtained by the thermolysis of compound I using this method contains Pt (~30 wt %), Pt<sub>3</sub>Fe (~40 wt %), and Fe<sub>3</sub>O<sub>4</sub> (~20 wt %). Iron oxide is formed due to contact with air oxygen after the sample was taken from the reactor.

Thermal curves for DCS I-III and initial Tschugaeff's salt are shown in Fig. 4. The results can conveniently be analyzed using published data [9] on the thermal stability of oxalate complexes of various transition metals. Potassium trioxalatoferrate(III) decomposes at 230-265°C to evolve CO<sub>2</sub>. Tschugaeff's salt starts to decompose with ammonia evolution at ~150°C, and the main step of decomposition begins at 250-260°C and ends the formation of metallic platinum. The superposition of these thermal curves gives an approximate image of the thermal curve for salt I. The first step is the dehydration of the complex, and the second step corresponds (by its weight loss) to the elimination of two  $CO_2$  molecules. This step coincides in temperature with the transformation of the complex into a black intermediate upon decomposition in hydrogen. Then, the decomposition of the coordination sphere of chloropentaammineplatinum occurs. The thermal curve for salt III can be characterized using the thermal curves for potassium trioxalatochromate(III) and Tschugaeff's salt. The first step represents the dehydration of the complex, and three water molecules fall per formula unit. Then, a prolong step of complete



decomposition of the compound to the final product occurs, and according to literature data [8], CO should be evolved along with  $CO_2$ .

Potassium oxalatocobaltate(III) starts to decompose at a lower temperature; therefore, both the dehydration of the complex and the decomposition of the oxalate anion occur at the first step in the thermal curve of salt **II**. The thermal curves presented show that complexes **I** and **II** have lower end temperatures of decomposition than complex **III** and Tschugaeff's salt. This can be explained by higher oxidative capabilities of iron and cobalt in the decomposition intermediates compared tochromium There is an analogy with an increase in the oxidation potential for the three-charged ions in the series  $Cr^{3+} \longrightarrow Fe^{3+} \longrightarrow Co^{3+}$ , as for the oxalate complexes [8]. The decomposition ends at 305°C for complexes I and II and at 425°C for salt III.

The final products of DCS decomposition in an inert atmosphere contain metallic platinum and oxide phases of base metals, whereas the decomposition product of complex I also contains an insignificant amount of a solid solution of  $Pt_{0.5}Fe_{0.5}$ .

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