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Synthesis and thermal decomposition of the oxalatho cuprates(II) – $[M(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$, M = Pt, Pd

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Abstract. The compounds $[Pd(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$ (1) and $[Pt(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$ (2) have been synthesized by crystallization from aqueous solutions. Both compounds are ionic salts and are isostructural, crystallising in space group I222). Thermal decomposition under He and H_2 atmosphere of titled compounds has been studied. Depending on conditions (temperature, heating rate and time), the final products of thermal decomposition are ordered or disordered solid solutions $Cu_{0.5}Pt_{0.5}$ and $Cu_{0.5}Pd_{0.5}$.

Introduction

Controlling the size, shape and phase composition of nanocrystalline materials is a key issue in current nanoscience research. Synthetic chemical methods have proved very effective for the production nanocrystals with a tight size distribution. These nanostructures exhibit very interesting magnetic, electrical, optical, and chemical properties, which cannot be achieved by the corresponding bulk materials [1-3]. Despite resent advances in synthesizing metal nanostructures with controlled morphologies, there are few reports where bimetallic nanoparticles containing platinum have been described: Pt-Co, Pt-Fe, Pt-Cu, Pt-Ni [4-6].
CoPt nanostructures have previously been successfully synthesized in solution-phase process by the use of a high boiling point coordinating solvent, reducing agent and nonionic surfactants that play the role of growth controllers and offer solubility in nonpolar organic solvents. An alternative method is the thermal decomposition of an organometallic precursor which provides directly, without the use of reducing agent, the Co partner for the formation of the CoPt bimetallic nanoparticles [4, 7]. Another way to prepare the bimetallic nanoparticles is thermal decomposition of the bimetallic molecular and salt-like precursors. For example, in [8, 9] it was described the preparation nanosized NiPt and PtRu powders by thermal decom-

position $[Ni(bipy)_3][PtCl_6]$ and $PtRu_5C(CO)_{16}$ or $Pt_2Ru_4(CO)_{18}$. In our previous reports we described properties of the metallic nanoparticles prepared by thermal decomposition of the double complex salts (DCS) $[M^1(NH_3)_5Cl][M^2Hal_4]$ (M^1 = Rh, Ir, Co, Cr, Ru; M^2 = Pt, Pd; Hal = Cl, Br) [10]. Such approaches allow us to prepare nanoparticles with different metals compositions.

In this paper we report synthesis details, crystal structure and thermal properties of salts with planar cations $[Pd(NH_3)_4]^{2+}$ or $[Pt(NH_3)_4]^{2+}$ and octahedral anion $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$. Final products depending on thermal decomposition conditions are single-phase metallic Pd-Cu and Pt-Cu solid solutions or intermetallic compounds.

Experimental section

General

$[Pd(NH_3)_4]Cl_2$, $[Pt(NH_3)_4]Cl_2$ and $(NH_4)_2[Cu(C_2O_4)_2]$ were synthesized as described previously.[11]. Thermogravimetric analyses (TG) were performed on Paulic-Paulic-Erdey Q-1000 instrument in flowing He or air (14 cm^3/min) with heating rate 10.0 K/min in silica crucibles. Infrared spectra were collected on Scimitar FTS 2000 as KBr pellets. X-ray powder data for the complexes and thermolysis products were taken on DRON-RM4 diffractometer (R = 192 mm, CuK_α radiation, graphite monochromator) over the 2θ range from 5° to 120° at room temperature. The refinement of lattice parameters was performed by the full profile technique applied to full-range diffraction data using PowderCell 2.4 program [12]. Crystallite sizes of the metal phases were determined by Fourier decomposition of profiles of single diffraction peaks, and with the Scherrer equation (WINFIT 1.2.1 [13]). Suitable single-crystals of (1) and (2) were selected and mounted on a BRUKER X8APEX CCD diffractometer (Mo-tube; K_α, λ = 0.7107 Å; graphite monochromator). The structures were solved by the standard heavy-atom method; anisotropic displacement parameters were refined. The SHELX97 program package [14] was used in all computations.

Synthesis of $[Pd(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$ (1)

Hot water solutions of 150 mg $[Pt(NH_3)_4]Cl_2$, (0.61 mmol in 10 ml) and 170 mg $(NH_4)_2[Cu(C_2O_4)_2]$ (0.62 mmol in 10 ml) were mixed. After 1 day azure needles were precipitated with a yield of 50 - 58 % based on Pd. Elemental analysis calculations found for $C_4H_{16}O_{10}N_4CuPd$: Pd + Cu 36.30 (36.3 ± 0.1) %. The crystal data for compound (1) were $C_4H_{16}O_{10}N_4CuPd$, M = 468.17, space group I222, a = 6.7176(2), b = 7.4318(2), c = 14.9682(5) Å, V = 747.27(4) $Å^3$, T = 293(2) K, Z = 2, Dcalc = 2.081, Dm = 2.08 ± 0.01g/cm^3, crystal dimensions 0.04×0.04×0.05 mm, R_1 = 0.0213, wR_2 = 0.0517 for 1801 reflections with $I > 2\sigma(I)$, and R_1 = 0.0200, wR_2 = 0.0511 for all 1742 reflections.

Synthesis of $[Pt(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$ (2)

Hot water solutions of 200 mg $[Pt(NH_3)_4]Cl_2$, (0.6 mmol in 10 ml) and 180 mg $(NH_4)_2[Cu(C_2O_4)_2]$ (0.65 mmol in 10 ml) were mixed. After 1 day azure needles were precipitated with a yield of 55-60 % based on Pt. Elemental analysis calculations found for $C_4H_{16}O_{10}N_4CuPt$: Pt + Cu 46.45 (46.4 ± 0.1) %. The crystal data for compound (2) were $C_4H_{16}O_{10}N_4CuPt$, M = 556.83, space group I222, a = 6.7376(3), b = 7.4110(3), c = 14.9891(5) Å, V = 748.44(5) $Å^3$, T = 293(2) K, Z = 2, Dcalc = 2.444, Dm = 2.5 ± 0.1g/cm^3,

crystal dimensions 0.04×0.04×0.05 mm, $R_1 = 0.0181$, $wR_2 = 0.0366$ for 1336 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0183$, $wR_2 = 0.0368$ for all 1338 reflections.
Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail crysdata@fiz-karlsruhe.de) on quoting depository numbers CSD 417074 (of $[Pd(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$ (1)) and CSD 417075 (of $[Pt(NH_3)_4][Cu(C_2O_4)_2]*3H_2O$ (2))

Results and discussion

Crystal Structures. Bought compounds (1) and (2) were characterized by single-crystal X-ray analysis. X-ray structural analysis revealed that the both compounds are isostructural and they are simple salts. The crystal structures are composed from planar cations $[Pd(NH_3)_4]^{2+}$ or $[Pt(NH_3)_4]^{2+}$, octahedral oxalate anions $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$ and molecules of crystallize water. Cations and anions packed together in a layered NaCl-type arrangement (figure 1).

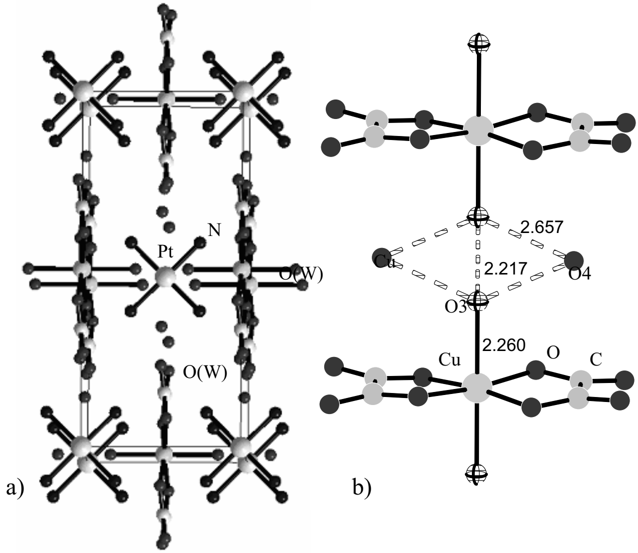

Figure 1. a) View down [101] of the structure of (2). Hydrogen atoms have been omitted for clarity. b) Fragment of the crystal structure (2) showing O…O hydrogen bonds between $[Cu(C_2O_4)_2(H_2O)_2]^{2+}$ cations and crystal water molecules. Dotted atom – disordered crystal water molecules. O…O distances in 1 are O3…O3 - 2.005, O3…O4 - 2.623, Cu…O3 2.357 Å

Each cation $[Pd(NH_3)_4]^{2+}$ or $[Pt(NH_3)_4]^{2+}$ is octahedrally surrounded by six $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$ anions and vice versa. Cations and anions have crystallographically imposed symmetry 222. Molecules of crystal water have crystallographically imposed symmetry positions 2. One of these is ordered (-0.3508, 0, 0.5), and second (which is coordinated to Cu) is disordered over two positions (0.5, 0, 0.33803). Two water ligands in $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$ octahedron are disordered, Cu…O distances in such anions are shown on figure 1. The geometrical imposed details of the $[Pd(NH_3)_4]_{2+}$ and $[Pt(NH_3)_4]^{2+}$ cations and $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$ anions of the structures do not differ significantly from the results of earlier determinations. Cu—O distances in (1) are 1.939 (1.946 in 2); Pd—N are 2.041 in (1) (Pt—N are 2.048 Å in 2); O—Cu—O angles are 85.76 and 94.24 in (1) (86.03 and 94.42° in 2). O…N distances between cationic NH_3 groups and anionic oxalate C=O groups are 3.089 and 3.127 Å in (1) (3.078 and 3.151 Å in 2). O…N distances between cationic NH_3 groups and water molecules are 4.080 Å in 1 (4.109 Å in 2). O…O distances between anionic oxalate C=O groups are 3.508 Å in (1) (3.516 Å in 2). Pd…O (in anion) distances are 4.352-4.376 Å; Pt…O (in anion) distances are 4.272-4.459 Å.

Thermal properties and final products of thermal decomposition in helium atmosphere. The thermogravimetric diagram of (1) (figure 2) shows that the first stage of weight loss (12 %), occurring about at 100-110 °C, corresponds to the complete loss of 3 molecules of water of crystallization (calculated: 11.5 %). An intermediate product of the thermal decomposition of (1) was prepared at 150 °C. A well-crystalline anhydrous product $[Pd(NH_3)_4][Cu(C_2O_4)_2]$ having unknown crystal structure was obtained (νH_2O and $\delta_d H_2O$ frequencies have disappeared from the IR spectrum, while other frequencies are identical to that of the hydrated product).

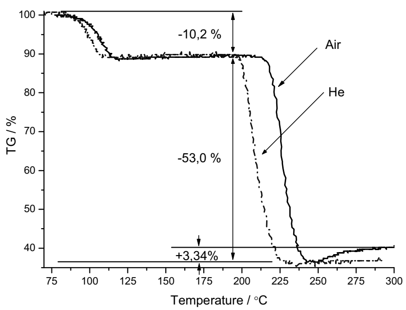

Figure 2. TG curves for $Pd(NH_3)_4][Cu(C_2O_4)_2]$ $3H_2O$ (in He and air).*

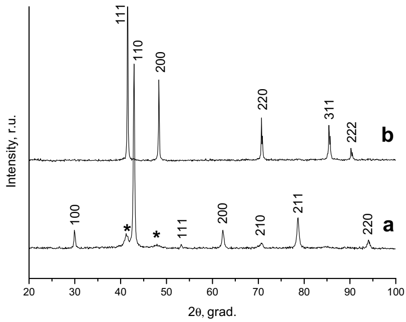

*Figure 3. XRD pattern of thermolysis products of $[Pd(NH_3)_4][Cu(C_2O_4)_2]$*$3H_2O$ (in He): a) mixture of intermetallic phase $Pd_{0.95}Cu_{1.05}$ and disordered fcc solid solution $Pd_{0.60}Cu_{0.40}$ (marked - *), b) disordered solid solution $Pd_{0.50}Cu_{0.50}$.*

Further decomposition in He takes place about 190-230 °C (in air at 225-240 °C). The weight of the residue is 36.4 % (calculated: 36.30 %). The final product is an ultrafine powder of black color. Powder diffraction pattern of this sample (figure 3) is indicative of the presence of two phases: a cubic intermetallic phase $Pd_{0.95}Cu_{1.05}$, space group Pm-3m, and a minor amount of a disordered fcc solid solution $Pd_{0.60}Cu_{0.40}$ (table 1). The composition of these phases was determined from atomic volumes ($v=V_{cel}/z_{at.}$) using an experimental results derived from the data of [15-20] (figure 4). The estimated uncertainty of the composition determination is 5 at.%. Simultaneous occurrence of two phases in the sample is in general agreement with the phase diagram of the palladium-copper system [21]. Subsequent annealing of the obtained sample in vacuum at higher temperature (400 ºC) during 12 h afforded a single-phase disordered solid solution $Pd_{0.50}Cu_{0.50}$ (figure 3), also in accord with the phase diagram of the system. (In air at 250-300 ºC the metallic products were oxidized to a Pd + $CuPdO_2$ mixture.)

Table.1. Properties of products of thermolysis in helium and hydrogen atmosphere.

Products of decomposition or annealing	Preparation conditions	Space group	Lattice parameters, Å		V/z, Å^3	Crystallite size, Å
			a	*c*		
$Pd_{0.95}Cu_{1.05}$ + $Pd_{0.60}Cu_{0.40}$	He, 300°C, 10.0 K/min	Pm-3m + Fm-3m	2.981(2) 3.789(8)	- -	13.25(1) 13.60(3)	200-250 50-80
$Pd_{0.50}Cu_{0.50}$ disordered	Vacuum, 400°C, 12 h	Fm-3m	3.765(3)	-	13.34(1)	200-250
$Pt_{0.50}Cu_{0.50}$ partially ordered	He, 390°C, 10.0 K/min	Fm-3m	3.795(6)	-	13.66(2)	50-70
$Pt_{1.0}Cu_{1.0}$ ordered	Vacuum, 400°C, 12 h	R-3m	2.700(4)	12.918(13)	13.60(2)	200-400
$Pd_{0.95}Cu_{1.05}$ + $Pd_{0.65}Cu_{0.35}$	H_2, 350 °C, 1 h	Pm-3m + Fm-3m	2.981(2) 3.797(8)	- -	13.25(1) 13.69(2)	200-350 90-180
$Pd_{0.50}Cu_{0.50}$ disordered	H_2, 500 °C, 1 h	Fm-3m	3.768(3)	-	13.37(1)	120-220
$Pt_{1.0}Cu_{1.0}$ ordered	H_2, 500 °C, 1 h	R-3m	2.700(4)	12.987(13)	13.67(2)	100-150
$Pt_{1.0}Cu_{1.0}$ ordered	H_2, 500 °C, 9 h	R-3m	2.698(4)	12.909(13)	13.56(2)	250-300

Thermal decomposition of (2) in He is similar. The first weight loss occurs about at 80-220 °C. Further decomposition happens at 270-390 °C. The product of decomposition is an ultrafine single-phase black-colored powder. The weight of the residual fraction is 46.4 % (calculated: 46.45 %). Powder diffraction pattern of this sample is illustrated in fig. 5.

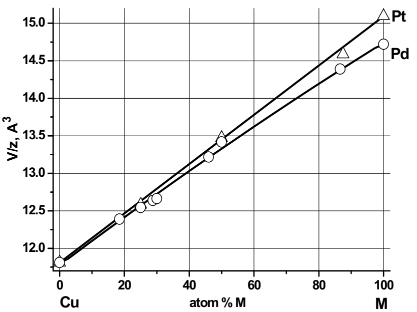

Figure 4. Plot of atomic volume versus concentration of the solid solutions.

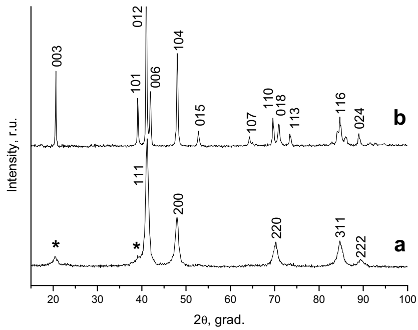

Figure 5. XRD pattern of $Pt(NH_3)_4][Cu(C_2O_4)_2]$ $3H_2O$ thermolysis products (in He): a) partly ordered $Pt_{0.50}Cu_{0.50}$ solid solution, b) intermetallic compound $Pt_{1.0}Cu_{1.0}$.*

The indexing of the major body of the peaks corresponds to the fcc crystal lattice of the platinum-copper solid solution. The composition of the solid solution - $Pt_{0.50}Cu_{0.50}$ – was determined in the manner described above for palladium-copper alloys, the experimental relationship between atomic volume and composition based on the data of [16, 22] being employed (table 1, fig. 4). A significant broadening of the peaks was attributed to small sizes of crystallites (50-70 Å) formed in precursor decomposition. Strain contribution into broadening of diffraction peaks is generally low in the case of powders prepared under such conditions. Also, in the pattern there are two weak and strongly broadened superstructural peaks at 22.44º and 39.29º 2θ, indicating partial ordering of the solid solution. However, no splitting of the basal peaks of the fcc lattice was observed. Subsequent annealing of the sample obtained in vacuum at 400 ºC during 12 h caused further ordering of the solid solution and formation of the $Pt_{1.0}Cu_{1.0}$ intermetallic compound with rhombohedral unit cell, space group R-3m (table 1, fig. 5). Crystal parameters and preparation conditions of the metallic phases are summarized in Table 1.

Products of thermal decomposition of the complexes in hydrogen atmosphere.
Thermal decomposition of (1) in hydrogen atmosphere at 350 °C, similarly to decomposition of this compound in helium at 300 ºC, allowed us to obtain a mixture of intermetallic compound $Pd_{0.95}Cu_{1.05}$ and a disordered solid solution $Pd_{0.65}Cu_{0.35}$. One hour annealing in hydrogen at 500 °C afforded a single-phase disordered solid solution $Pd_{0.50}Cu_{0.50}$. As expected, higher temperatures and longer times of annealing result in larger crystallites, however, their sizes remain below 300 Å under these conditions.
Reduction of the compound (2) in hydrogen during 1 h at 500ºC yields an ultrafine single-phase powder of intermetallic compound $Pt_{1.0}Cu_{1.0}$ (crystallite size 100-150 Å). Additional annealing of the sample during 8 h at the same temperature does not essentially affect the unit cell parameters (table 1), but the crystallite size is doubled.

Summary

It has been demonstrated that the DCS combining platinum or palladium in the cation and copper in the anion can be used as single-source molecular precursors of nano-sized alloys: thermal decomposition of the compounds in helium and hydrogen results in formation of ultrafine bimetallic powders having equimolar metal ratio.
It is of importance that a small size of bimetallic particles originating from thermal decomposition of the DCS at comparatively low temperatures determines high kinetic activity of them. The processes of formation and decomposition, as well as ordering of these solid solutions proceed in few hours, while analogous transformations of bulk samples at higher temperatures (>600ºC) take dozens of hours [23, 24].

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