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Double complex salts of Pt and Pd ammines with Zn and Ni oxalates – promising precursors of nanosized alloys

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Abstract

Double complex salts $[M(NH_3)_4][M'(Ox)_2(H_2O)_2] \cdot 2H_2O$ (M = Pd, Pt, M' = Ni, Zn) were synthesized by combination of solutions containing corresponding cations $[M(NH_3)_4]^{2+}$ and anions $[M'(Ox)_2(H_2O)_2]^{2-}$. The salts obtained were characterized by IR spectros-copy, thermal analysis, powder and single crystal X-ray diffraction. The prepared compounds are isostructural and crystallize in the orthorhombic crystal system (space group *I*222, *Z* = 2). Thermal decomposition of the salts in helium or hydrogen atmosphere at 200–400 °C results in formation of nano-sized bimetallic powders. Depending on the phase diagram of the respective bimetallic system and temperature conditions, they can be single phase or multiphase products. In particular, thermal decomposition of double complex salts $[M(NH_3)_4][Zn(Ox)_2(H_2O)_2] \cdot 2H_2O$ (M = Pd, Pt) results in formation of PdZn and PtZn intermetallic compounds, correspondingly. Decomposition of $[Pd(NH_3)_4][Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$ affords a disordered solid solution $Pd_{0.5}Ni_{0.5}$. Disordered $Pt_{0.5}Ni_{0.5}$ was obtained from $[Pt(NH_3)_4][Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$ in helium atmosphere, while in hydrogen atmosphere – a two-phase mixture of disordered $Pt_{0.5}Ni_{0.5}$ and ordered PtNi. In all cases crystallite sizes of bimetallic particles varied within 50–250 Å. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Development of new approaches to preparation of nano-sized particles is highly topical for the systems based on such particles gain increasing role in fundamental research and applications [1–6]. Nano-sized materials comprising bimetallic particles often exhibit very intriguing optical, magnetic, electric and chemical properties [7]. A particularly characteristic feature of the particles of this type is the synergetic effect of atoms of different types in catalysts.

There are several methods of preparation of such powders, refer, for example, to [8-11]. One of the most common approaches to the synthesis of the desired metallic system is simultaneous decomposition or reduction of two precursor compounds. However, this widely used approach suffers serious drawbacks, such as radial composition heterogeneity of the developing particles (core-shell particles) or aggregation of atoms of different types into separate phases. The technique utilizing single-component precursor compounds, in particular, double complex salts containing one of the metals in the complex cation, and the other – in the complex anion, suggests a number of advantages for the following reasons.

First, in the complex precursor the metals are uniformly distributed ("mixed") at the molecular level, making the preparation of a single-phase solid solution much easier.

Second, the stoichiometry of the precursor complex strictly determines the composition of the bimetallic phase being formed. Thus, decomposition of double complex salts (DCS) $[Ir(NH_3)_5Cl]_2[ReCl_6]Cl_2$, $[Ir(NH_3)_5Cl][ReCl_6]$,

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[Ir(NH₃)₅Cl](ReO₄)₂ yields solid solutions Ir_xRe_{1-x} with component ratios 2:1, 1:1, 1:2, respectively [12,13]. Moreover, the accessible compositions of bimetallic particles are not just limited to stoichiometrical ratios of the components. For example, earlier we have prepared a series of mutual solid solutions of DCS [Ir(NH₃)₅Cl][ReCl₆] and [Ir(NH₃)₅Cl][IrCl₆] having the following compositions – [Ir(NH₃)₅Cl][IrCl₆]_x[ReCl₆](1-x) (x = 0, 0.4, 0.8) [12,14]. On decomposition of these compounds there are formed solid solutions Ir_{(1+x)/2}Re(1-x)/2 corresponding to the predetermined metal ratio in the complex.

Furthermore, due to comparatively low thermolysis temperatures, the powders being formed have a high degree of dispersion (50–250 Å). Because of the small size, the developed bimetallic particles reveal high activity in diverse chemical reactions.

Finally, synthesis of the precursor compounds can be carried out directly on the surface of various porous materials, thus opening prospects for preparation of novel catalysts [15]. When preparing supported bimetallic catalysts, the lowering of thermolysis temperature of the precursor compound, achieved by selection of proper ligands, is a major concern. Besides, DCS must be free from halogens, sulfur, and other catalytic poisons. Therefore, ammonia molecules and oxalate ions are the most preferable and handy ligands for these purposes.

2. Experimental

2.1. Syntheses

All compounds were prepared with the same technique described in detail below for $[Pt(NH_3)_4][Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$.

2.1.1. $[Pt(NH_3)_4][Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$, (hereafter abbreviated as [Pt-Ni] for the sake of brevity)

The starting $[Pt(NH_3)_4]Cl_2$ was prepared from platinum metal by the standard technique [16]. Anionic complex $(NH_4)_2[Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$ was not isolated as a solid. A solution of NiSO₄ was treated with an equimolar amount of aqueous (NH₄)₂Ox to yield NiOx precipitate. The precipitate was collected on a filter, washed, and dissolved in twofold excess of aqueous (NH₄)₂Ox, the resulting solution of $(NH_4)_2[Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$ being further used for the synthesis of DCS. To prepare [Pt-Ni], a solution of $[Pt(NH_3)_4]Cl_2$ (1 mmol) in a minimal amount of water was mixed with the solution of $(NH_4)_2[Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$ (10% molar excess). The precipitate resulted from the reaction was filtered off, washed with ethanol and dried in air. The product obtained was characterized with a number of physical chemical methods. CHN analyses was carried out in Laboratory of Microanalysis of Vorozhtsov Institute of Organic Chemistry SB RAS, Novosibirsk, Russia.

Yield: 68%. *Anal.* Calc. for C₄H₂₀N₄O₁₂PtNi: (Pt+Ni), 44.53; C, 8.43; H, 3.54; N, 9.83. Found: (Pt+Ni), 44.5; C,

8.39; H, 3.52; N, 9.63%. Selected IR spectral data (KBr, cm^{-1}): 3269 vb, 1651 s, 1435 m, 1350 s, 1300 s, 904 m, 787 m, 717 m, 516 w, 487 m, 389 w.

2.1.2. $[Pd(NH_3)_4][Ni(Ox)_2(H_2O)_2] \cdot 2H_2O$ (**[Pd-Ni]**)

Yield: 39%. Anal. Calc. for $C_4H_{20}N_4O_{12}PdNi$: (Pd+Ni), 34.30; C, 9.98; H, 4.19; N, 11.64. Found: (Pt+Zn), 45.1; C, 10.39; H, 4.38; N, 11.44%. Selected IR spectral data (KBr, cm⁻¹): 3283 vb, 1648 s, 1433 m, 1301 s, 850 m, 789 m, 718 m, 505 sh, 483 m, 384 w.

2.1.3. $[Pt(NH_3)_4]/[Zn(Ox)_2(H_2O)_2] \cdot 2H_2O([Pt-Zn])$

Yield: 82%. Anal. Calc. for $C_4H_{20}N_4O_{12}PtZn$: (Pt+Zn), 45.17; C, 8.62; H, 3.27; N, 9.61. Found: (Pt+Zn), 45.1; C, 8.33; H, 3.50; N, 9.72%. Selected IR spectral data (KBr, cm⁻¹): 3273 vb, 1650 s, 1432 m, 1351 s, 1301 s, 902 m, 784 m, 714 m, 514 w, 491 m, 392 w.

2.1.4. $[Pd(NH_3)_4][Zn(Ox)_2(H_2O)_2] \cdot 2H_2O([Pd-Zn])$

Yield: 72%. Anal. Calc. for $C_4H_{20}N_4O_{12}PdZn$: (Pd+Zn), 35.21; C, 9.84; H, 4.13; N, 11.48. Found: (Pd+Zn), 35.5; C, 10.11; H, 4.24; N, 11.32%. Selected IR spectral data (KBr, cm⁻¹): 3286 vb, 1651 s, 1432 m, 1302 s, 851 m, 789 m, 723 m, 514 w, 487 m, 392 w.

2.2. Single crystal and powder X-ray diffraction analysis

Blue (M' = Ni) and white (M' = Zn) needle crystals of the DCS were grown by slow evaporation of their mother liquors. Single crystal X-ray diffraction study was carried out on a BRUKER X8 APEX CCD diffractometer at room temperature using graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å). The structures were solved by the standard heavy atom method and refined in anisotropic approximation. All calculations were performed with SHELX97 program package [17]. Crystal data and experimental details are given in Table 1, selected bond lengths and angles are listed in Table 2.

Polycrystalline samples were studied on a DRON-RM4 powder diffractometer equipped with a Cu K α source ($\lambda = 1.5418$ Å) and graphite monochromator at the diffracted beam in 2θ range 5–120°. Indexing of the diffraction patterns was carried out using data for pure metals and compounds reported in the PDF database [18]. Unit cell parameters were refined by the full-profile technique within the whole diffraction range with the POWDERCELL 2.4 program [19]. Crystallite sizes in the prepared bimetallic powders were determined by Fourier analysis of single diffraction peaks (the program WINFIT 1.2.1 [20]).

2.3. Scanning electron microscopy

Scanning electron microscopy study of the samples was made on a JEOL JSM 6700F device equipped with a dispersive X-ray analyzer EX-23000BU (EDS) operating 15 kV.

Table 1 Selected distances and angles for $[M(NH_3)_4]\![M'(Ox)_2(H_2O)_2]\cdot 2H_2O$

	Double complex salt						
	[Pt–Ni]	[Pt–Zn]	[Pd-Ni]	[Pd-Zn]			
Empirical formula	C ₄ H ₂₀ N ₄ NiO ₁₂ Pt	$C_4H_{20}N_4O_{12}PtZn$	C ₄ H ₂₀ N ₄ NiO ₁₂ Pd	C ₄ H ₂₀ N ₄ O ₁₂ PdZn			
Formula weight	570.00	576.69	481.34	488.03			
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic			
Space group	<i>I</i> 222	<i>I</i> 222	<i>I</i> 222	<i>I</i> 222			
a (Å)	7.162(1)	7.237(7)	7.154(1)	7.214(1)			
b (Å)	7.182(1)	7.177(0)	7.204(1)	7.214(1)			
<i>c</i> (Å)	15.037(2)	15.083(1)	15.014(1)	15.070(3)			
Ζ	2	2	2	2			
$V(Å^3)$	773.58(3)	783.43(5)	773.88(2)	784.44(3)			
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	2.447	2.445	2.066	2.066			
$\mu (\mathrm{mm}^{-1})$	10.315	10.514	2.444	2.740			
<i>F</i> (000)	548	552	484	488			
Θ range	3–35	3–38	3–37	5-30			
Reflections collected	3845	2648	1795	754			
Independent reflections	1644	1019	1566	752			
Parameters	63	66	74	62			
Goodness-of-fit	1.035	1.111	1.090	1.048			
$R_1, wR[I > 2\sigma(I)]$	0.0193, 0.0461	0.0153, 0.0392	0.0274, 0.0572	0.0199, 0.0587			
R_1 , wR (all data)	0.0193, 0.0461	0.0153, 0.0392	0.0335, 0.0601	0.0200, 0.0588			
$\Delta \rho_{\min}$ and $_{\max}$ (e Å ⁻³)	1.784, -2.867	1.361, -0.737	1.086, -1.255	0.510, -0.649			

The salts are denoted as [M-M'].

Table 2	
Crystal data and experimental characteristics for	$[M(NH_3)_4][M'(Ox)_2(H_2O)_2] \cdot 2H_2O$

	Distances (Å)		Angles (°)		Angles (°)
[Pt-Ni]					
Pt–N1	2.0460(22)	N1″-Pt-N1	179.879(87)	O1-Ni-O1'''	97.976(69)
Ni–O1W	2.0141(36)	N1–Pt–N1′	91.321(87)	O1–Ni–O1′	82.031(69)
Ni-O1	2.0390(18)	N1"-Pt-N1'	88.679(87)	C1–O1–Ni	112.845(160)
O1–C1	1.2669(30)	O1W–Ni–O1W′	179.983(83)	O2-C1-O1	126.660(232)
O2–C1	1.2317(31)	O1W–Ni–O1	89.577(261)	O2-C1-C1′	117.202(217)
C1C1'	1.5600(31)	O1W'-Ni-O1	90.423(261)	O1–C1–C1′	116.138(188)
		O1-Ni-O1"	179.155(67)		
[Pt-Zn]					
Pt–N1	2.0457(25)	N1″-Pt-N1	179.986(121)	O1–Zn–O'''1	98.623(82)
Zn-O1W	2.0672(40)	N1–Pt–N1′	91.635(106)	O1–Zn–O1′	81.377(82)
Zn-O1	2.0683(28)	N1″-Pt-N1′	88.365(106)	C1–O1–Zn	112.911(170)
O1–C1	1.2695(39)	O1W–Zn–O1W'	180.000(225)	O2-C1-O1	127.103(246)
O2C1	1.2307(46)	O1W–Zn–O1	88.439(67)	O2-C1-C1′	116.510(296)
C1C1'	1.5681(66)	O1W'-Zn-O1	91.561(67)	O1–C1–C1′	116.387(261)
		O1–Zn–O1″	180.000(104)		
[Pd-Ni]					
Pd–N1	2.0427(21)	N1″–Pd–N1	178.626(81)	O1-Ni-O1'''	98.264(50)
Ni–O1W	2.0160(29)	N1–Pd–N1′	91.619(81)	O1–Ni–O1′	81.774(50)
Ni-O1	2.0341(13)	N1″–Pd–N1′	88.397(81)	C1–O1–Ni	113.100(105)
O1–C1	1.2641(21)	O1W–Ni–O1W′	179.982(66)	O2C1O1	126.595(157)
O2C1	1.2287(21)	O1W–Ni–O1	88.972(220)	O2-C1-C1'	117.254(137)
C1–C1′	1.5564(21)	O1W'-Ni-O1	91.028(220)	O1–C1–C1′	115.891(133)
		O1-Ni-O1"	177.944(50)		
[Pd-Zn]					
Pd–N1	2.046(3)	N1″–Pd–N1	179.4(7)	O1–Zn–O1′′′	99.22(14)
Zn-O1W	2.062(4)	N1–Pd–N1′	91.55(16)	O1–Zn–O1′	80.95(13)
Zn-O1	2.070(2)	N1″–Pd–N1′	88.45(16)	C1–O1–Zn	112.9(2)
O1–C1	1.262(4)	O1W–Zn–O1W'	180.000	O2C1O1	125.8(3)
O2–C1	1.229(4)	O1W–Zn–O1	87.8(4)	O2-C1-C1′	117.2(3)
C1C1'	1.558(6)	O1W'–Zn–O1	92.2(4)	O1–C1–C1′	116.58(18)
		O1–Zn–O1″	175.7(8)		

The salts are denoted as [M-M'].

able 3	
hase composition, heating temperatures and crystallite size of thermolysis products of $[M(NH_3)_4][M'(Ox)_2(H_2O)_2]$.	$2H_2O$

Precursor salt	Atmosphere	T_{\max} (°C)	Phase	Space group	a (Å)	<i>c</i> (Å)	Crystallite size (nm)
[Pt-Ni]	He	400	Pt _{0.5} Ni _{0.5}	Fm-3m	3.760(4)		6–8
	H_2	475	$Pt_{0.5}Ni_{0.5} +$	Fm-3m	3.753(3)		10-14
			PtNi	P4/mmm	2.705(2)	3.620(3)	10–14
[Pd-Ni]	He	400	Pd _{0.5} Ni _{0.5}	Fm-3m	3.754(4)		6–8
	H_2	250	Pd _{0.5} Ni _{0.5}	Fm-3m	3.745(3)		7–10
[Pt-Zn]	He	450	PtZn	P4/mmm	2.848(3)	3.516(4)	5-8
	H_2	300	PtZn	P4/mmm	2.858(2)	3.465(3)	9–13
[Pd-Zn]	He	360	PdZn	P4/mmm	2.908(3)	3.318(4)	5-8
	H_2	300	PdZn	P4/mmm	2.897(2)	3.343(3)	11–24

The salts are denoted as [M-M'].

2.4. Thermal analysis

Prepared DCS were studied on a Paulic-Erdey Q-1000 derivatograph equipped with digital output, Al_2O_3 powder being used as the standard. The experiments were run in an open silica crucible in helium stream at heating rate 10 °C/min. The final temperatures of the experiments are reported in Table 3.

2.5. Decomposition in hydrogen atmosphere

To synthesize bimetallic powders in hydrogen atmosphere weighted samples of DCS (\sim 50 mg) were placed in a silica boat and put in a tubular silica reactor. Heating was performed in a split furnace at the rate of 20 °C/min. After reaching the final temperature (Table 3), samples were kept for 1 h, and then the hydrogen stream was switched off and the system was purged with helium during 30 min. Afterwards the heater was removed and the reactor was allowed to cool to ambient temperature in continuous helium stream.

3. Results and discussion

3.1. Crystal structure

X-ray diffraction study of the crystals revealed that all new compounds are isostructural. Fig. 1 schematically illustrates the general view of the unit cell. The crystals of DCS are built from isolated complex ions shown in Fig. 2.

The atoms of nickel (zinc) have octahedral environment of six oxygen atoms. The distances $M'-O_{ox}$ and $M'-O_{w}$ are almost identical differing at most by 0.02 Å (Table 2). Because of the rigidity of the chelate ligands the octahedral $[M'O_6]$ lack symmetry – in the equatorial plane the *trans*angles deviate from 90 and make $82.03(7)^{\circ}$ and $97.97(7)^{\circ}$. The atoms of platinum (palladium) are square-coordinated with four nitrogen atoms. The adjacent angles between the



Fig. 1. Common view of the unit cell of DCS. Complex cations $[M(NH_3)_4]^{2+}$ are shown as dark squares, chelate planes $[M'Ox_2]^{2-}$ are shown as light rectangles with two coordinated molecules of water.



Fig. 2. The detailed structure of complex ions.

M–N bonds are different from 90° resulting in a slight distortion of the planar-square cations.

As evident from Fig. 1, there are two types of water molecules in the structure. Each atom of nickel (zinc) coordinates two water molecules in the *trans*-positions. Besides, a pair of crystallization water molecules is present at each ac and bc faces of the unit cell. The molecules of the water of crystallization lie in the plane of the chelate ligands of the complex anions and make hydrogen bonds to the terminal oxygen atoms (O2). The distances $H(W)_{cryst}$ -O2 are



Fig. 3. The illustration of hydrogen bonds between structural units in DCS.

Table 4 Hydrogen bonds by example of interatomic distances A \ldots B in D–H \ldots B system

Suit	[I* t–INI]	[Pd-Ni]	[Pt–Zn]	[Pd-Zn]
Contacts				
Crystal water stal	bilization			
01W02W	2.750(3)	2.743(2)	2.748(3)	2.706(3)
O2O2W	2.696(3)	2.706(2)	2.698(3)	2.738(3)
Cation stabilization	on			
N101	3.106(9)	3.111(9)	3.121(1)	3.182(13)
N101′	3.082(9)	3.097(9)	3.110(1)	3.058(13)
N1O2	3.052(7)	3.030(6)	3.052(7)	3.088(10)

within 1.85–2.00 Å. In turn, the coordinated water molecules are joined by hydrogen bonds with the crystallization water molecules, the distances $H(W)_{coord}$ – $O(W)_{cryst}$ being 1.95–2.20 Å. Thus, crystallization water molecules and the complex cations are stabilized by the complex anions by virtue of hydrogen bonding. Average distances O...O and O...N are 2.7 and 3.1 Å, what is characteristic of strong bonding in such systems. Fig. 3 and Table 4, listing the distances between the atoms A and B in the D–H...B system, illustrate the situation.

Mutual arrangement of the complex anions, as determined using the central atoms (Fig. 4), indicates that each complex ion is surrounded by six complex counter ions. Therefore, the DCS crystallize in the distorted structural type of NaCl.

As found with powder X-ray diffraction, all precipitates of the compounds obtained are single-phase. Experimental diffraction patterns of the polycrystalline samples coincide with theoretical ones and do not have additional reflections.



Fig. 4. The mutual arrangement of central atoms in DCS. The unit cell is drawn with dotted line.

3.2. Thermal properties

In inert atmosphere the thermal behavior of all new DCS is similar. The overall thermogram is shown in Fig. 5. As one can see, all compounds decompose in two major stages. The first one corresponds to the complete loss of water. Weight loss (72-75 Da) is in a good accordance with the calculated value for four water molecules (72 Da). Above, we have noted that one half of water molecules are coordinated by nickel (zinc) atoms, while the other is linked with the complex anions only with hydrogen bonds. One could suppose that the coordinated water molecule and the crystallization water molecule would evolve in separate steps, but this resolution into two stages is observed only for [Pd-Ni]. The heated products, according to IR spectroscopy data, do not contain water, but retain the bands corresponding to the vibrations of the ammonia and oxalate ligands. We did not succeed in identifying these phases because these products are being amorphous.

The temperatures of decomposition onset for the DCS and the corresponding dehydrated products are shown in Fig. 6. It also presents the temperatures of decomposition onset of diaqua oxalates of nickel and zinc $M'Ox \cdot 2H_2O$, as well as of tetraammineplatinum and tetraamminepalladium perrhenates $[M(NH_3)_4](ReO_4)_2$ (M = Pt, Pd) [21,22]. On the basis of the data obtained, three regularities can be derived. First, as evident from the plot, zinc DCS begin to loose water at lower temperatures than nickel DCS. This correlates with available data on the thermal stability of $M'Ox \cdot 2H_2O$ undergoing dehydration in the same priority due to the differences in the strength of the bonds Zn-OH₂ and Ni-OH₂.

The second stage corresponds to complete decomposition of the complexes to the bimetallic products. One can conclude that the thermal stability of the anhydrous products is primarily governed by the thermal stability of the complex cation, as DCS comprising the cation $[Pd(NH_3)_4]^{2+}$ begin to decompose earlier than DCS containing the cation



Fig. 5. Combined TG-pattern for $[M(NH_3)_4][M'(Ox)_2(H_2O)_2] \cdot 2H_2O$ (M = Pt, Pd, M' = Zn, Ni). The complex salts are denoted as [M-M'].



Fig. 6. Temperatures of thermal stability for $[M(NH_3)_4][M'(Ox)_2(H_2O)_2] \cdot 2H_2O$ (M = Pt, Pd, M' = Zn, Ni), M'Ox $\cdot 2H_2O$ (M'=Zn, Ni), anhydrous products of corresponding salts and $[M(NH_3)_4][ReO_4)_2$ (M = Pt, Pd). The complex salts are denoted as [M-M']. White symbols represent the temperatures of dehydration beginning; black symbols represent the temperatures of the beginning of further full decomposition.

 $[Pt(NH_3)_4]^{2^+}$. This agrees with the fact that platinum(II) complexes are generally more stable than corresponding palladium(II) complexes. This fact is illustrated by the example of $[M(NH_3)_4](ReO_4)_2$, which begin to degrade from decomposition of the $[M(NH_3)_4]^{2^+}$ cations while ReO_4^- anions remain intact [21,22], and the palladium salt also being decomposed first.

However, the nature of the complex anion is also of importance. Among the prepared DCS containing the same cation, the salts involving nickel are less stable due to its higher oxidative potential. Lower decomposition temperatures of the dehydrated nickel oxalates support this fact.

3.3. Products of thermolysis

All synthesized DCS were subjected to heating in helium and hydrogen atmospheres. Heating in hydrogen was carried out at 20 K/min rate, after the target temperature had been reached; the sample was kept in the gas stream for another hour. Heating in helium atmosphere was performed 7 K/min rate. After achieving the desired temperature, the sample was cooled to ambient temperature in a helium stream during 1 h. The products were examined with powder XRD and EDS. Annealing temperatures, phase composition and crystal chemical data for the samples are given in Table 3.

The product obtained by thermal decomposition of the DCS [Pt–Ni] in helium at 400 °C is a single-phase fine black powder of the solid solution $Pt_{0.5}Ni_{0.5}$, which has the FCC unit cell parameter a = 3.760(3) Å. The value of the unit cell parameter found for this solid solution is in a good agreement with that determined from the experimental dependence of the unit cell parameter of the solid solution on its composition derived from the data of [23–25] (Fig. 7a).

During reductive thermolysis of the DCS [Pt-Ni] in hydrogen atmosphere the final temperature was raised to 475 °C. According to the phase diagram of the platinumnickel system [26], a field of an ordered solid solution exists below 650 °C. As a consequence, the alloy obtained has undergone partial ordering to yield the intermetallic compound. The final product is two-phased and comprises the disordered solid solution (a = 3.753(3) Å) and the intermetallic PtNi (space group P4/mmm, a = 2.705(2) Å, c = 3.620(3) Å). As reported in Ref. [27], unit cell parameters of the intermetallic compound are a = 2.711(2) Å, c = 3.602(2) Å, and Ref. [28] gives a = 2.698(2) Å, c = 3.582(2) Å. Powder diffraction pattern of the sample is illustrated in Fig. 8. The composition of the sample was confirmed by energy dispersive X-ray spectroscopy (EDS).

It is noteworthy that the shape of metallic particles inherits the habitus of the original crystals of DCS. However, subsequent scans with growing resolution reveal that the particles are built from smaller blocks with the sizes of ~ 10 nm (see Fig. 9).



Fig. 7. Experimental dependence of atomic volume vs solid solution composition for system Ni–Pt (a) Ni–Pd (b). Literature date are marked by black points, data of this work are marked by light one's.



Fig. 8. XRD pattern of PtNi intermetallic and $Pt_{0.5}Ni_{0.5}$ solid solution mixture, ^ – peaks of PtNi intermetallic, * – peaks of $Pt_{0.5}Ni_{0.5}$ solid solution.

Thermolysis of the **[Pd–Ni]** DCS, both in helium and in hydrogen, afforded single-phase samples of the disordered solid solution palladium–nickel. The values of the unit cell parameter of the FCC cell, found for these solid solutions, are slightly above the value a = 3.741 Å derived for the solids solution Pd_{0.5}Ni_{0.5} from experimental dependence of the unit cell parameter on the composition of the solid solution [29,18,30–32] (Fig. 7b, Table 3).

For the systems Pt–Zn and Pd–Zn, the thermolysis of starting DCS both in helium and in hydrogen gave single-phase samples of intermetallic compounds PtZn and PdZn, respectively, which have the tetragonal crystal lattice of the CuAu type, space group *P4/mmm* (Table 3).

This method of preparation of nano-sized particles enables to control the sizes of the developing particles by proper tuning of the thermolysis conditions (temperature, duration, and heating rate). Thus, the intermetallic PtZn can be obtained as particles of average size 10 nm (300 °C, 10 E/min, exposure 1 h). When decomposition temperature is raised to 400 °C, the particle size reaches 25 nm. Longer exposure of samples to a preset temperature also promotes the growth of the particles: when the sample prepared at 400 $^{\circ}$ C (25 nm) was kept in a sealed quartz ampoule for another 12 h, particle size increased to 40 nm.

PtNi, PdNi and Pd-Zn samples manifest the same tendencies.

High chemical activity of bimetallic particles prepared by DCS decomposition also has a negative aspect. The surface of the particles is partially oxidized by atmospheric oxygen as evidenced by EDS data. However, the amount of the adsorbed oxygen is negligible. When exposed to air for several weeks, the products do not show any changes in weight.

4. Conclusion

Novel double complex salts combining a platinum metal in the cation and base transition metal in the anion have been prepared. The synthesized complexes have been shown to be isostructural. It has been demonstrated that the compounds can be used as single-source precursors of nano-sized alloys: thermal decomposition of the compounds in helium and hydrogen results in formation of ultrafine bimetallic powders with varying metal ratios.

It is noteworthy that during thermolysis of a double complex salt comprising a platinum metal, zinc can be reduced to yield the intermetallic compound, while common zinc salts do not afford metal even under reduction in hydrogen atmosphere.

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Appendix A. Supplementary material

Crystallographic data from the structural analyses have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail crysdata@fiz-karlsruhe.de)



Fig. 9. Microphotographs of obtained PtNi particles was to carried out by SEM. (a) Shows that shape of metal particles inherits a habitus of initial crystals of DSC [Pt–Ni]. But if to increase the resolution it can be see that bulk particles consist of smaller blocks which are about 100 nm in size (b).

on quoting depository numbers CSD 417562 (of [Pd–Ni]), CSD 417563 (of [Pd–Zn]), CSD 417564 (of [Pt–Ni]) and CSD 417565 (of [Pt–Zn]). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.07.006.

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