Supporting Information for

the manuscript "Complex Salts of Pd(II) and Pt(II) with Co(II) And Ni(II) Aquocations as Single-Source Precursors for Bimetallic Nanoalloys" by Andrey Zadesenets, Evgeniy Filatov, Pavel Plyusnin, Tatyana Asanova, Iraida Baidina, Elena Slyakhova, Igor Asanov and Sergey Korenev

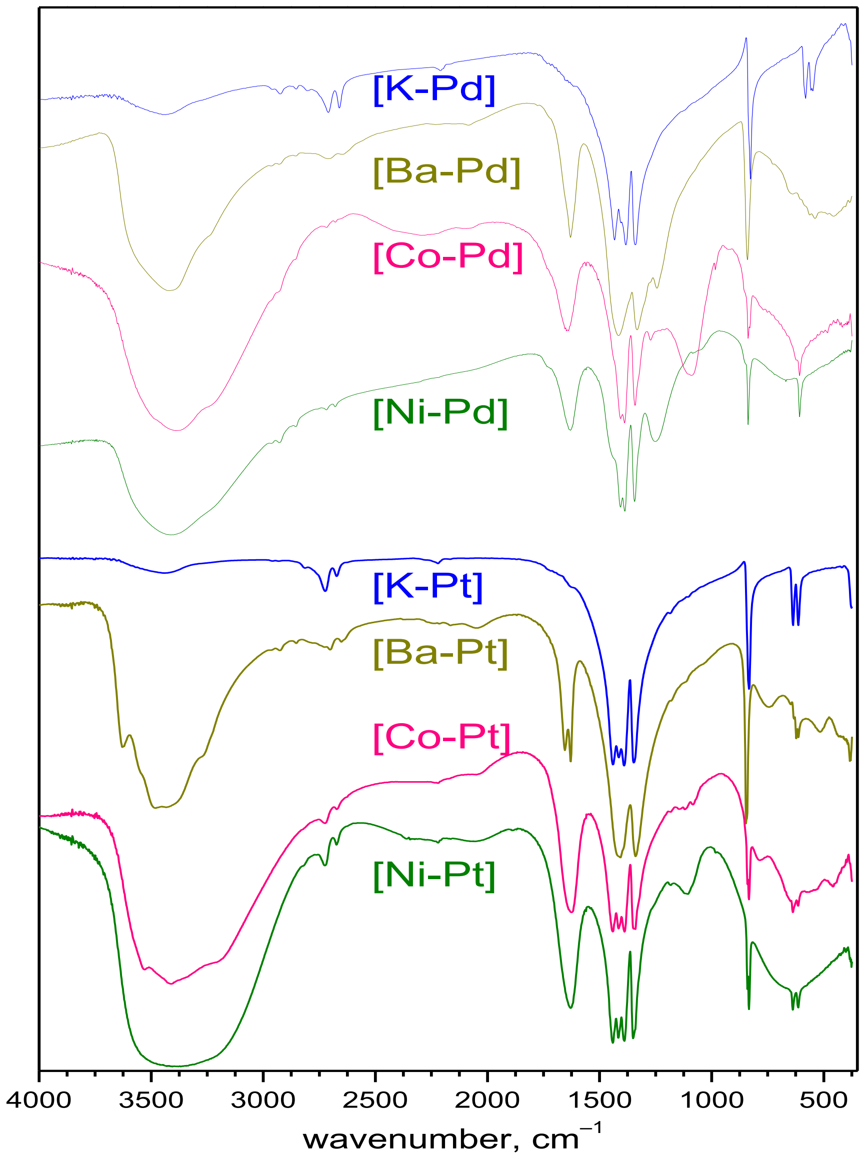


Figure 1s. IR-spectra of DCSs and related nitrocomplex salts of Pd.

$Ba[Pt(NO_2)_4]\cdot 3H_2O$ (ν, cm^{-1}): 3469 ν(H_2O); 1628 δ(H_2O); 1413, 1336 ν(NO_2^-); 846 δ(ONO);
$[Co(H_2O)_6][Pt(NO_2)_4]\cdot 2H_2O$: 3412 ν($H_2O$); 1624 δ($H_2O$); 1440, 1415, 1388 $\nu_a(NO_2^-)$; 1348 $\nu_s(NO_2^-)$, 840, 833 δ(ONO); 636, 613 $\rho_w(NO_2^-)$;
$[Ni(H_2O)_6][Pt(NO_2)_4]\cdot 2H_2O$: 3367 ν($H_2O$); 1628 δ($H_2O$); 1440, 1415, 1388 $\nu_a(NO_2^-)$, 1350 $\nu_s(NO_2^-)$, 833 δ(ONO); 638, 613 $\rho_w(NO_2^-)$;
$[Co(H_2O)_6][Pd(NO_2)_4]\cdot 2H_2O$: 3389 ν($H_2O$); 1647 δ($H_2O$); 1440, 1406, 1389 $\nu_a(NO_2^-)$, 1342 $\nu_s(NO_2^-)$, 837 δ(ONO); 608 $\rho_w(NO_2^-)$;
$[Ni(H_2O)_6][Pd(NO_2)_4]\cdot 2H_2O$: 3410 ν($H_2O$); 1630 δ($H_2O$); 1436, 1406, 1387 $\nu_a(NO_2^-)$, 1344 $\nu_s(NO_2^-)$, 829, 837 δ(ONO); 608 $\rho_w(NO_2^-)$;

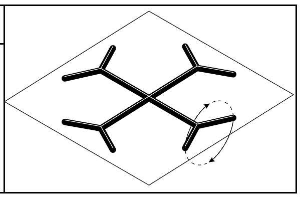
Table 1s. Crystallografic data of [M'-M''].

Compound	[Ba-Pt]	[Co-Pd]	[Ni-Pd]	[Co-Pt]	[Ni-Pt]
Crystal system	triclinic				
Sppace group	P−1				
a, Å	8.3841(7)	6.0051(3)	5.9834(2)	5,9125(4)	5.9377(4)
b, Å	8.4220(7)	7.8865(4)	7.8788(3)	7.8201(5)	7.7854(5)
c, Å	9.5643(8)	8.6872(5)	8.6406(3)	8,7149(6)	8.7147(5)
α, °	81.036(2)	110.055(3)	110.211(2)	110,076(3)	110.031(3)
β, °	71.001(2)	105.100(3)	105.344(2)	103,908(3)	104.303(3)
γ, °	60.479(2)	96.203(3)	95.988(2)	96,272(3)	96.242(3)
V, Å^3	555.65(8)	364.18(3)	359.90(2)	359.15(4)	358.39(4)
Z	2	1			
ρ_{calc}, g·cm^{-3}	3.410	2.250	2.276	2.691	2.696
Absorption coefficient	16.158	2.465	2.650	10.973	11.155
F (000)	512	245	246	276	278
T, K	296(2)	296(2)	296(2)	296(2)	296(2)
Reflections collected	7763	9020	6655	4018	6420
Independent reflections	2364	5211	4146	2656	3476
R(int)	0.0278	0.0367	0.0323	0.0234	0.0267
2θ, °	2.25 – 31.18	3.60 – 33.17	2.65 – 33.19	2.61 – 30.49	2.61 – 32.13
Parameters/restraints	182/9	248/19	261/11	210/24	248/19
Goodness-of-fit on F^2	1.073	1.008	1.101	0.6117	1.038
R1, wR2 (*all data*)	0.0157, 0.0380	0.0247, 0.0493	0.0229, 0.0506	0.0234, 0.6117	0.0148, 0.0346
R1, wR2 ($I>2\sigma$)	0.0152, 0.0378	0.0211, 0.0479	0.0212, 0.0497	0.0234, 0.6117	0.0148, 0.0346
№ ICSD	1590231	1590234	1590233	1590230	1590228

Table 2s. Selected distances and angles for DCSs.

Compound	[Ba-Pt]	[Co-Pd]	[Ni-Pd]	[Co-Pt]	[Ni-Pt]
Distances					
M'–OW1 *[Ba-Pt]: Ba…O1W	2.770(2)	2.144(5)	2.070(6)	2.11(2)	2.074(8)
M'–OW2 *[Ba-Pt]: Ba…O2W	2.742(3)	2.106(5)	2.099(5)	2.05(2)	2.079(7)
M'–OW3 *[Ba-Pt]: Ba…O3W	2.741(3)	2.073(5)	2.056(5)	2.13(2)	2.024(8)
M'–OW4		2.055(6)	2.052(5)	2.14(2)	2.032(8)
M'–OW5		2.080(5)	2.041(6)	2.04(2)	2.077(9)
M'–OW6		2.095(5)	2.021(6)	2.09(2)	2.017(9)
M''–N1	2.020(3)	2.043(5)	2.023(4)	2.052(2)	2.011(7)
M''–N2	2.012(2)	2.022(4)	1.999(5)	2.058(2)	2.020(9)
M''–N3 *[Ba-Pt]: Pt2–N3	2.005(3)	2.022(6)	2.047(4)	1.977(2)	2.035(6)
M''–N4 *[Ba-Pt]: Pt2–N4	2.024(3)	2.026(5)	2.038(5)	1.975(2)	1.987(9)
N1–O1		1.201(7)	1.220(7)	1.21(3)	1.247(9)
N1–O2		1.217(7)	1.243(7)	1.29(2)	1.213(9)
N2–O3		1.206(7)	1.238(7)	1.20(2)	1.238(9)
N2–O4		1.261(7)	1.248(7)	1.24(3)	1.214(9)
N3–O5		1.242(7)	1.232(6)	1.24(2)	1.247(9)
N3–O6		1.265(8)	1.237(6)	1.29(3)	1.191(9)
N4–O7		1.215(8)	1.221(6)	1.30(2)	1.257(9)
N4–O8		1.263(7)	1.220(7)	1.25(3)	1.247(9)
Angles					
OW1–M'–OW2 *[Ba-Pt]: O1W–Ba–O2W	131.5(1)	177.6(3)	178.1(3)	176.9(8)	179.3(5)
OW1–M'–OW3 *[Ba-Pt]: O1W–Ba–O2W	75.08(11)	91.7(2)	88.6(2)	86.6(8)	90.6(3)
OW1–M'–OW4 *[Ba-Pt]: O1W–Ba–O2W	126.26(8)	88.5(2)	91.1(2)	91.4(7)	89.2(3)
OW1–M'–OW5		92.8(2)	89.7(2)	91.1(8)	90.8(3)
OW1–M'–OW6		88.3(2)	92.4(2)	93.0(8)	89.0(4)
OW2–M'–OW3		88.0(2)	90.3(2)	90.4(8)	89.6(3)
OW2–M'–OW4		91.8(2)	90.0(2)	91.5(7)	90.6(3)
OW2–M'–OW5		89.6(2)	91.8(2)	88.2(8)	88.5(3)
OW2–M'–OW6		89.3(2)	86.1(2)	87.9(8)	91.7(4)
OW3–M'–OW4		179.5(4)	179.7(3)	178.0(8)	179.7(6)
OW3–M'–OW5		91.0(2)	92.1(2)	95.6(9)	93.1(4)
OW3–M'–OW6		87.8(2)	89.5(2)	88.6(9)	87.2(4)
N1–M''–N2 *[Ba-Pt]: N1–Pt1–N2	86.3(1)	87.3(2)	87.1(2)	86.2(3)	86.7(5)
N1–M''–N3 *[Ba-Pt]: N1–Pt1–N1'	180.00	178.6(3)	179.5(3)	178.1(4)	175.9(8)
N1–M''–N4 *[Ba-Pt]: N2–Pt1–N1'	93.7(1)	93.0(2)	92.9(2)	93.6(3)	91.2(6)
N2–M''–N3 *[Ba-Pt]: N3–Pt2–N4	89.4(1)	92.5(2)	93.0(2)	92.3(3)	95.0(6)
N2–M''–N4 *[Ba-Pt]: N3–Pt2–N3'	180.00	178.6(3)	179.5(3)	179.7(4)	176.4(8)
N3–M''–N4 *[Ba-Pt]: N4–Pt2–N3'	90.6(1)	87.2(2)	87.0(2)	87.8(3)	87.3(7)
O1–N1–O2	118.4(3)	121.1(5)	118.6(4)	118.5(8)	122.7(18)
O3–N2–O4	118.9(2)	119.0(5)	118.2(5)	120.9(10)	124.8(17)
O5–N3–O6	119.1(3)	116.3(6)	119.2(4)	120.1(7)	113.6(17)
O7–N4–O8	118.0(3)	120.6(5)	120.6(5)	117.3(10)	112.8(16)

Table 3s. Rotation angles of NO_2-groups relative to [M''N_4]-plane in [M''$(NO_2)_4$]$^{2-}$ anions (clockwise).

Axis	[Co-Pd]	[Ni-Pd]	[Co-Pt]	[Ni-Pt]	
N1–M''	66.0(3)	66.7(3)	57.4(8)	62.7(5)	
N2–M''	54.2(3)	55.7(3)	53.1(9)	54.0(5)	
N3–M''	−63.0(3)	−63.6(3)	−66.0(9)	−61.5(5)	
N4–M''	−55.8(3)	−54.1(3)	−54.7(9)	−53.7(5)	

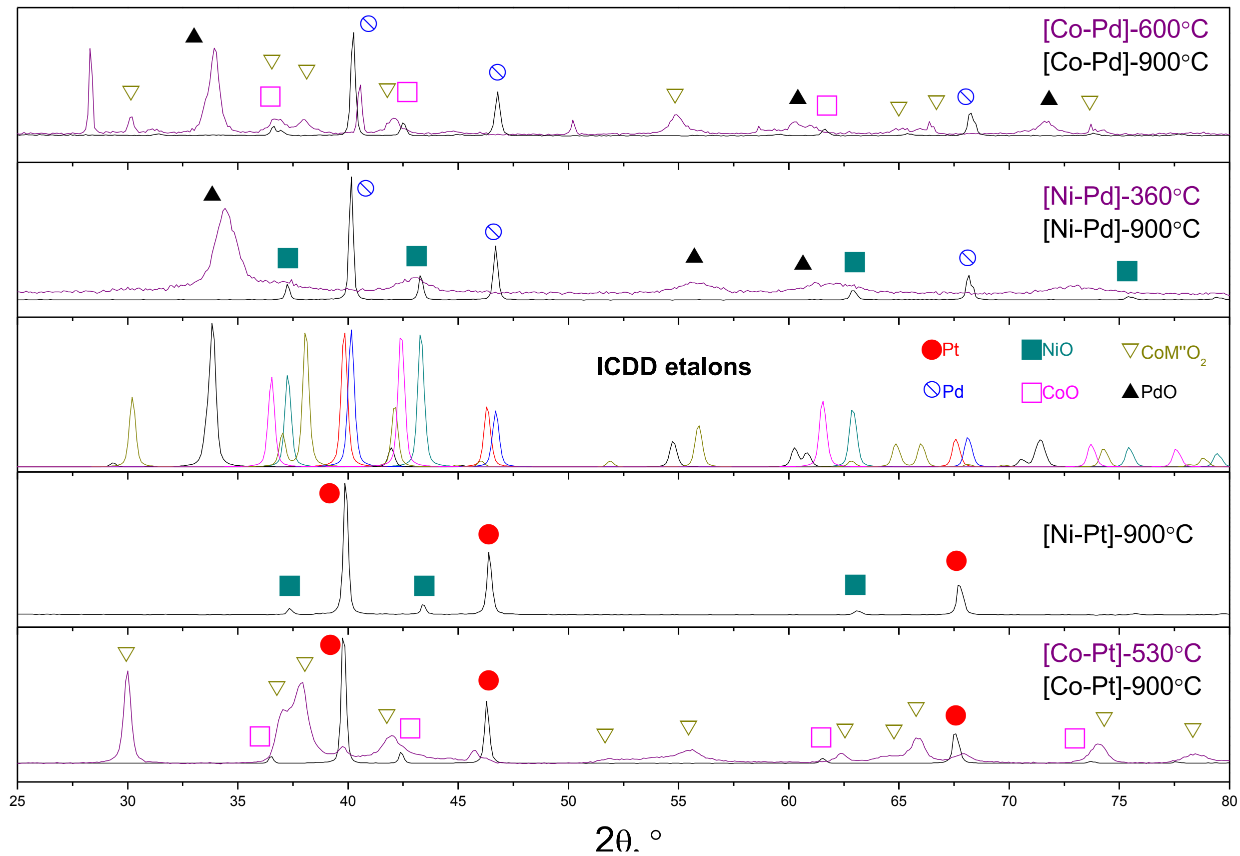


Figure 2s. XRD patterns of decomposition products in He.

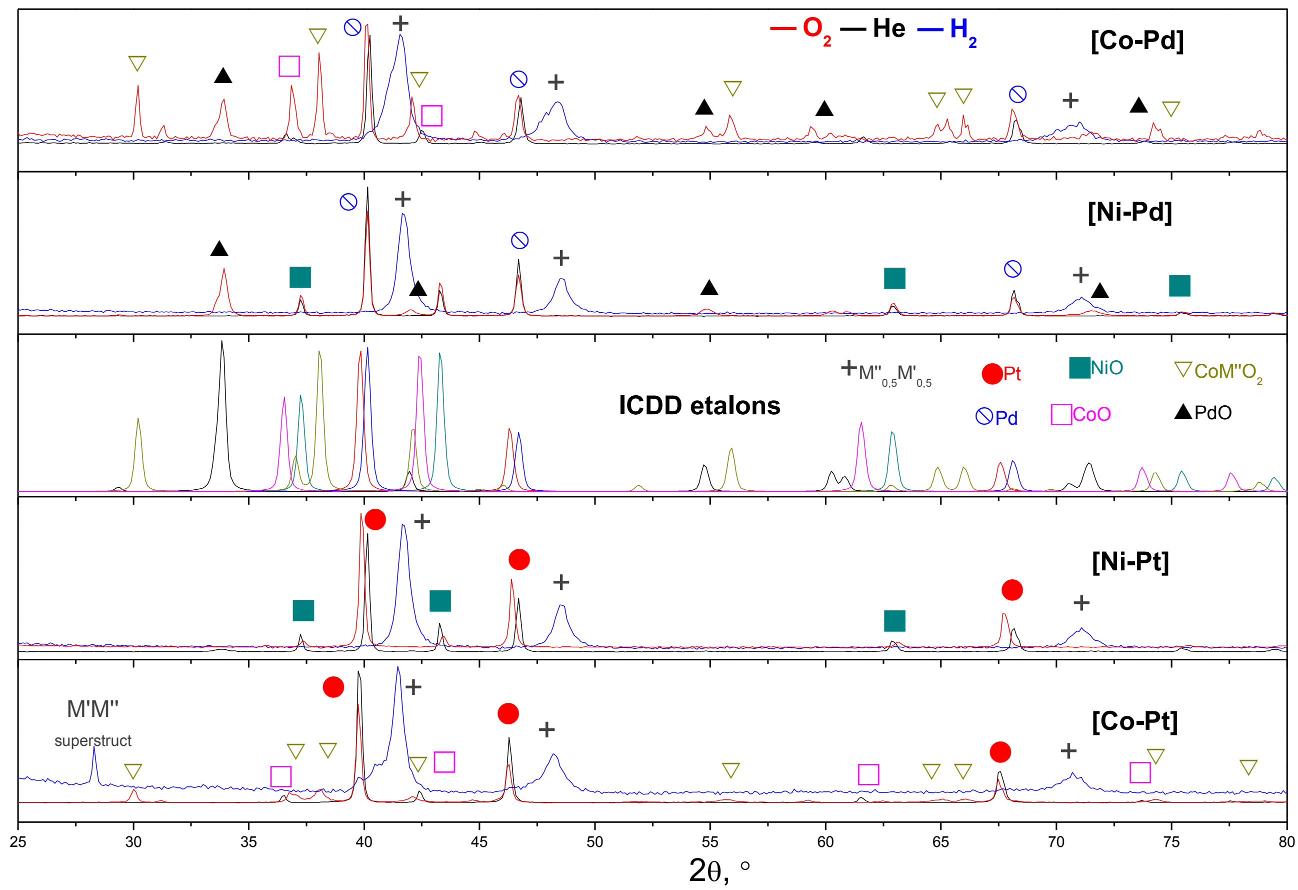


Figure 3s. XRD patterns of final decomposition products in He, O_2 and H_2.

3.2.3. XPS of [Co-Pt] and oxide semi-products. Before discussing the XPS results some elucidations about CoO and Co_3O_4 must be done. The surface of CoO is always oxidized to Co_3O_4.[1] Moreover, the Co binding energies in various oxides and hydroxides overlap, it is also possible an overlap of oxide satellites with metallic Co $2p_{1/2}$. The easiest to distinguish CoO from Co_3O_4 is by profile of spectrum, namely intensity of satellite. The CoO intensity is much greater than that of Co_3O_4.

The Co $2p_{3/2,1/2}$ spectrum of initial DCS (**Figure 4**) can be described by two doublets with a splitting of 15.2 eV. The first two peaks of Co $2p_{3/2}$ are at 782.2 and 786.6 eV, the first one is regarded to Co(II), the second one is charge transfer satellite. The spectrum of Pt $4f_{7/2,5/2}$ is a doublet with a splitting of 3.3 eV. In DCS the position of Pt $4f_{7/2}$ is at 74 eV and the position of N 1s is 404.9, that corresponds to Pt(II)-N binding energy in $[Pt(NO_2)_4]^{2-}$ complex. The O 1s spectrum consists of two peaks. One of them (533.4 eV) is regarded to oxygen which is bonded to Co; the second one (532.4 eV) – to NO_2^-.

The spectrum of a sample, which was obtained by heating of DCS up to 400 °C, is characteristic for CoO[2] The spectrum of O 1s consists of two lines at 530.4 and 531.6 eV. The first one is typical for metal oxides, the second can be referred to C–O groups (surface CO_3^{2-}).[3] The spectrum of Pt contains three doublets with Pt $4f_{7/2}$ at 72.9, 74.2 and 75.1 eV. Binding energies of 74.2 and 75.1 eV correspond to Pt(II) and Pt(IV) and can be ascribed to PtO- and PtO_2-like phases.[4] The peak at 72.9 eV is in between Pt(0) and Pt(II). The similar line was observed by other authors[5,6] and can be explained by a partial reduction of Pt(IV) to Pt(I) and decrease of coordination number, since gradually arising $PtCoO_2$ phase comprises of Pt(I) and Co(III).

The Co spectrum of 550 °C sample is being well described with a combination of lines referred to Co_3O_4. The formation of this oxide has to do primarily with the surface, and not with the volume due to above-mentioned reasons. Two doublets appear in the Pt spectrum with Pt $4f_{7/2}$ 72.2 and 74.0 eV. The line 74.0 eV is referred to Pt(II); the line 72.2 eV supposed to be analogous to that in 400 °C sample. As can be seen from 400 ° and 550 °C spectra, the peak of Pt $4f_{7/2}$ shifts a 0.6 eV to lower energy area with increase of temperature, and its intensity grows approximately twice. The shift of binding energies to lower values is due to Pt(I) fraction becomes the main in bulk mass. The O 1s spectrum comprises three components at 529.8, 531.2 and 532.9 eV, which can be attributed to O-Pt, O in CO_3^{2-} and OH^- respectively.

The Co spectrum of 700 °C is similar to that of 550 °C sample. The Pt $4f_{7/2}$ line (ascribed to Pt(I)) increases and continues to shift to Pt(0), the energy is 71.8 eV. The second component at 74.1 (ascribed to PtO-like phase) decreases. The spectra of O 1s changes insignificantly.

The Co spectrum of final product is intermediate between CoO and Co_3O_4. Since the CoO was confirmed by XRD, it could be partially oxidized at surface. The Pt spectrum is analogous to Pt(0). The O spectrum remains to comprise of three components: oxide, carbonate and hydroxide.

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