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## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Synthesis and Characterization of [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>][M(NO<sub>2</sub>)<sub>4</sub>] (M = Pt, Pd) Compounds and Their Thermolysis Products

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Abstract—Compounds  $[Co(NH_3)_5NO_2][Pd(NO_2)_4]$  (I) and  $[Co(NH_3)_5NO_2][Pt(NO_2)_4] \cdot 1.5H_2O$  (II) have been crystallized from solution. Their crystal structures have been solved, and thermolysis under various conditions studied. The thermolysis products are  $Co_{0.5}M_{0.5}$  ordered solid solutions.

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The syntheses and structures of double complex salts containing a complex cation and a complex anion have been studied for a sufficiently long time [1], but the study by Michelot and colleagues [2] has spurred interest in their thermolysis and final thermolysis products in various gas atmospheres. Michelot and colleagues [2] noticed that [Ir(NH<sub>3</sub>)<sub>5</sub>Cl][PtCl<sub>4</sub>] thermolysis under a hydrogen atmosphere finally yielded Ir<sub>0.5</sub>Pt<sub>0.5</sub> solid solution. The Ir<sub>0.5</sub>Pt<sub>0.5</sub> solid solution was formed after the salt was applied to alumina pellets and reduced in the support phase. Michelot and colleagues [2] also demonstrated that this support system can serve as a reforming catalyst.

Substituting nonprecious cobalt for precious iridium lowers the catalyst's cost and improves its characteristics [3]. Another way to improve the characteristics of the catalysts is to use precursor complexes free of halide ions. Here, we have synthesized and characterized such compounds:  $[Co(NH_3)_5NO_2][Pd(NO_2)_4]$  (I) and  $[Co(NH_3)_5NO_2][Pt(NO_2)_4] \cdot 1.5H_2O$  (II). Our efforts were directed to solving the structure of the complexes and studying their transformations under various conditions.

### **EXPERIMENTAL**

The starting chemicals used ( $[Co(NH_3)_5NO_2]Cl_2$ ,  $K_2[Pt(NO_2)_4]$ , and  $K_2[Pd(NO_2)_4]$ ) were prepared by procedures described elsewhere [4, 5].

Phases of the double complex salts were prepared as follows. A  $[Co(NH_3)_5NO_2]Cl_2$  sample (0.5 mmol) was dissolved in minimum hot water and mixed with a solution of  $K_2[M(NO_2)_4]$  (0.5 mmol) in minimum hot water. After some time, double complex crystals precipitated

in the form of yellow platelets for M = Pd or orange needles for M = Pt. The precipitate was allowed to stand for 10 min; then, it was vacuum filtered, washed with acetone, and dried in air. Yield: 75–85%.

Element analysis was by atomic absorption on a Hitachi Z800 spectrometer with Zeeman background correction. A salt aliquot was dissolved in water in the presence of hydrochloric acid under heating. The total of metals was determined by reducing the salt aliquot in flowing hydrogen in a boat inside a reactor (both made of fused silica).

The results of element analysis for compound **I** were as below.

For H<sub>15</sub>N<sub>10</sub>O<sub>10</sub>CoPd anal. calcd., %: Co, 12.26; Pd, 22.15; Co + Pd, 34.41.

Found, %: Co,  $11.2 \pm 0.5$ ; Pd,  $18.9 \pm 0.5$ ; Co + Pd,  $34.8 \pm 0.2$ .

The results of element analysis for compound **II** were as below.

For  $H_{18}N_{10}O_{11.5}$ CoPt anal. calcd., %: Co, 9.8; Pt, 35.2; Co + Pt, 41.61.

Found, %: Co, 9.6  $\pm$  0.5; Pt, 35.2  $\pm$  0.5; Co + Pt, 42.7  $\pm$  0.2.

The thermogravimetric properties of the compounds were studied on a Q-1000 derivatograph modified to operate in various gas atmospheres. A sample about 15 mg in size was mixed with a tenfold amount of  $Al_2O_3$  and transferred into a covered platinum crucible. The heating rate was 3 K/min in flowing helium (150 ml/min).

Polycrystal X-ray diffraction experiments were carried out for ethanol mulls applied to the polished side of a fused silica cell (DRON Seifert RM4,  $CuK_{\alpha}$  radiation,

Parameter	Ι	II	Atom	x/a	y/b
Formula weight	480.55	587.26	Pd(1)	7373(1)	4344(1)
<i>a</i> , Å	8.0209(8)	7.7583(8)	Co(1)	7019(1)	1598(1)
h Å	22,167(2)	9 6385(9)	N(1)	5904(10)	5083(3)
	7 9 4 5 2 (9)	10.0641(11)	O(11)	4512(10)	5096(3)
с, А	7.0433(8)	10.9041(11)	O(12)	6354(11)	5520(3)
α, deg	90	97.216(2)	N(2)	5551(10)	3822(3)
β, deg	98.836(2)	92.090(2)	O(21)	5952(9)	3567(3)
γ, deg	90	112.2500(10)	O(22)	4130(8)	3775(3)
Space group	Cc	$P\bar{1}$	N(3)	8787(8)	3591(3)
			O(31)	9116(9)	3228(3)
<i>V</i> , A <sup>3</sup>	1378.3(2)	749.66(13)	O(32)	9283(10)	3525(3)
Ζ	4	2	N(4)	9379(9)	4896(3)
$\rho_{calc}, g/cm^3$	2.316	2.602	O(41)	10554(17)	4748(4)
$\rho_{meas}$ , g/cm <sup>3</sup>	$2.29\pm0.01$	$2.70\pm0.02$	O(42)	8932(13)	5294(5)
θ range, deg	2.73-23.27	2.31-23.27	N(5)	6937(9)	2139(3)
Number of measured reflections	2661	3268	N(6)	7206(10)	884(3)
Number of unique reflections	1317	2662	N(7)	7082(9)	1073(3)
$P$ for reflections with $L > 2\pi(I)$	0.0247	0.0180	N(8)	9421(9)	1685(3)
<i>k</i> for reflections with $I > 20(I)$	0.0247	0.0180	N(9)	4522(9)	1522(3)
<i>wR</i> for reflections with $I > 2\sigma(I)$	0.0583	0.0443	N(10)	6738(9)	2280(3)
R for all reflections	0.0248	0.0189	O(101)	7611(10)	2340(3)
wR for all reflections	0.0584	0.0449	O(102)	5632(8)	2662(3)

**Table 1.** Crystal data and details of the X-ray diffraction experiment

**Table 2.** Atomic coordinates (×10<sup>4</sup>) and equivalent thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for complex I

 $U_{\rm eq}, {\rm \AA}^2$ 

22(1)

21(1)

35(2)

72(2)

66(2)

28(2)

46(2)

42(2)

23(2)

43(2)

54(2)

16(1)

97(3)

91(3)

27(2)

27(2)

26(2)

31(2)

33(2)

29(2)

46(2)

38(2)

z/c 4273(1)

4400(1)

4346(9)

3419(12)

5206(10)

5116(9)

6517(8)

4302(8)

4069(8)

5204(8)

2695(10)

3524(8)

4123(15)

2853(12)

6416(9)

5955(9)

2421(9)

4643(10)

4105(9)

2895(8)

1741(9)

3035(7)

graphite monochromator on the reflected beam, scintil-
lation detector with amplitude discrimination, frame
mode). A polycrystalline silicon sample ( $a = 5.4309 \text{ Å}$ )
prepared in the same manner was the external standard.
The 2 $\theta$ range was from 5° to 60° for the complex salt
and from $5^{\circ}$ to 135° for the thermolysis products.

The X-ray diffraction patterns were indexed completely on the basis of the single-crystal data; therefore, the samples were single phases. X-ray phase analysis was performed by analogy with X-ray diffraction patterns for pure metals and intermetallic compounds from the PDF file [6]. The parameters of the metal phases were refined over the entire data set using the Powder-Cell 2.3 program [7].

Single-crystal X-ray diffraction experiments were carried out (the unit cell parameters were refined, and the X-ray diffraction reflection intensities were measured in order to solve the crystal structures) on a Bruker AXS P4 diffractometer (Mo $K_{\alpha}$  radiation, graphite monochromator,  $\theta/2\theta$  scan mode, room temperature). The crystal data, experimental details, and refinement parameters are listed in Table 1. The structures were solved by the standard heavy-atom method and refined in the anisotropic approximation. The

SHELX97 program package [8] was used in all computations. The atomic coordinates in the structures of compounds I and II are listed in Tables 2 and 3. Selected bond lengths and bond angles are listed in Tables 4 and 5.

### **RESULTS AND DISCUSSION**

The method we developed for the synthesis of double complex salts allows us to prepare single crystals suitable for X-ray diffraction experiment. Double complex salts I and II have different crystal-water concentrations. Therefore, their structural features will be described separately.

**Crystal structure of**  $[Co(NH_3)_5NO_2][Pd(NO_2)_4]$ (**compound I**). A comparative crystal-chemical analysis of the compounds of the  $[Pd(NO_2)_4]^{2-}$  anion was carried out in [9]. The configuration of the anion was found to vary noticeably depending on the cation. Compound I contains a rather bulky complex cation capable of hydrogen bonding with the anion.

The compound crystallizes in yellow monoclinic platelets. The crystal structure is built of isolated

Atom	x/a	y/b	z/c	$U_{ m eq}$ , Å <sup>2</sup>
Pt(1)	-2976(1)	6671(1)	1761(1)	29(1)
Pt(2)	-5233(1)	3316(1)	-4705(1)	28(1)
Co(1)	2750(4)	8127(3)	6567(3)	24(1)
Co(2)	-10975(4)	1866(3)	459(3)	23(1)
N(11)	1580(20)	6252(15)	5362(15)	29(4)
N(12)	470(30)	8456(19)	6490(20)	60(6)
N(13)	1960(20)	6988(16)	7938(13)	38(5)
N(14)	5070(17)	7769(12)	6659(14)	21(3)
N(15)	3510(20)	9317(17)	5222(14)	36(4)
N(16)	3865(18)	9942(16)	7736(18)	33(5)
N(21)	-9830(20)	3800(18)	1666(16)	38(5)
N(22)	-8642(18)	1467(16)	498(15)	28(4)
N(23)	-13300(20)	2174(18)	389(16)	48(5)
N(24)	-10130(20)	2956(16)	-929(14)	43(5)
N(25)	-11810(20)	732(16)	1823(15)	40(5)
N(26)	-12170(30)	17(18)	-685(14)	35(5)
O(16A)	3140(20)	10123(17)	8655(16)	44(5)
O(16B)	5450(20)	10893(14)	7567(11)	37(4)
O(26A)	-11310(20)	-170(15)	-1634(15)	47(5)
O(26B)	-13637(19)	-943(14)	-487(15)	52(5)
N(1)	-5320(30)	5620(20)	620(20)	33(4)
N(2)	-1330(20)	6720(19)	422(18)	36(5)
N(3)	-4640(30)	6691(18)	3180(20)	78(8)
N(4)	-790(30)	7600(20)	2993(19)	42(5)
N(5)	-2970(30)	4370(20)	-3470(20)	45(5)
N(6)	-6930(20)	3293(17)	-3320(18)	33(4)
N(7)	-7670(30)	2370(20)	-5850(20)	47(5)
N(8)	-3580(20)	3360(20)	-6044(19)	55(6)
O(11)	-6350(20)	6166(17)	444(18)	51(4)
O(12)	-5590(20)	4342(18)	-2(15)	69(5)
O(21)	-1080(20)	5557(16)	-122(14)	56(5)
O(22)	-310(20)	7970(15)	89(18)	57(4)
O(31)	-5930(30)	5660(20)	3250(20)	100(6)
O(32)	-4630(18)	7934(14)	3522(12)	119(5)
O(41)	610(30)	7190(20)	2930(20)	113(8)
O(42)	-670(30)	8390(30)	3878(16)	167(11)
O(51)	-2590(30)	5680(19)	-3120(20)	102(8)
O(52)	-1700(20)	3810(20)	-3311(19)	63(5)
O(61)	-6920(20)	4467(16)	-2900(17)	61(5)
O(62)	-7810(20)	2127(17)	-3015(18)	66(6)
O(71)	-7930(30)	1200(20)	-6540(20)	203(15)
O(72)	-8779(18)	2769(17)	-5826(13)	50(4)
O(81)	-4510(20)	3158(18)	-7294(11)	144(6)
O(82)	-2140(30)	3800(40)	-6130(20)	186(14)
O(1W)	7790(30)	590(20)	5320(20)	133(9)
O(2W)	-6030(30)	-400(20)	-8487(15)	74(4)

**Table 3.** Atomic coordinates (×10<sup>4</sup>) and equivalent thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) for complex **II** 

Bond	<i>d</i> , Å	Angle	w, deg
Pd(1)–N(1)	2.025(7)	N(10)Co(1)N(8)	90.2(3)
Pd(1)–N(3)	2.037(7)	N(10)Co(1)N(7)	89.7(3)
Pd(1)–N(2)	2.052(8)	N(8)Co(1)N(7)	89.5(3)
Pd(1)–N(4)	2.173(7)	N(10)Co(1)N(9)	88.5(3)
Co(1)–N(10)	1.911(7)	N(8)Co(1)N(9)	178.6(3)
Co(1)–N(8)	1.916(7)	N(7)Co(1)N(9)	90.4(3)
Co(1)–N(7)	1.946(7)	N(10)Co(1)N(6)	177.6(3)
Co(1)–N(9)	1.988(7)	N(8)Co(1)N(6)	92.3(3)
Co(1)–N(6)	1.990(7)	N(7)Co(1)N(6)	90.3(3)
Co(1)–N(5)	1.995(7)	N(9)Co(1)N(6)	89.1(3)
N(1)–O(12)	1.204(10)	N(10)Co(1)N(5)	89.9(3)
N(1)–O(11)	1.236(10)	N(8)Co(1)N(5)	90.9(3)
N(2)–O(22)	1.222(10)	N(7)Co(1)N(5)	179.5(3)
N(2)–O(21)	1.233(9)	N(9)Co(1)N(5)	89.3(3)
N(3)–O(31)	1.199(8)	N(6)Co(1)N(5)	90.1(3)
N(3)–O(32)	1.214(9)	O(12)N(1)O(11)	118.5(8)
N(4)–O(41)	1.040(13)	O(12)N(1)Pd(1)	122.8(6)
N(4)-O(42)	1.061(12)	O(11)N(1)Pd(1)	118.7(6)
N(10)-O(101)	1.233(9)	O(22)N(2)O(21)	121.4(8)
N(10)-O(102)	1.243(9)	O(22)N(2)Pd(1)	122.2(6)
		O(21)N(2)Pd(1)	116.3(6)
Angle	ω, deg	O(31)N(3)O(32)	121.0(7)
N(1)Pd(1)N(3)	176.9(3)	O(31)N(3)Pd(1)	123.5(5)
N(1)Pd(1)N(2)	90.0(3)	O(32)N(3)Pd(1)	115.5(6)
N(3)Pd(1)N(2)	89.8(3)	O(41)N(4)O(42)	134.4(10)
N(1)Pd(1)N(4)	90.6(3)	O(41)N(4)Pd(1)	111.0(7)
N(3)Pd(1)N(4)	89.8(2)	O(42)N(4)Pd(1)	113.3(7)
N(2)Pd(1)N(4)	176.9(3)	O(101)N(10)O(102)	118.9(7)
O(101)N(10)Co(1)	120.9(6)	O(102)N(10)Co(1)	120.2(5)

**Table 4.** Bond lengths (*d*) and bond angles ( $\omega$ ) in the structure of I

 $[Co(NH_3)_5NO_2]^{2+}$  complex cations and  $[Pd(NO_2)_4]^{2-}$ anions; both species have no symmetry elements. The Pd atom is coordinated by the nitrogen atoms of the four nitro groups that form a slightly distorted square; the Pd–N bond lengths average 2.072 Å; the NPdN bond angles approach 90°. The PdN<sub>4</sub> coordination square is nearly planar; the departures of the atoms are within 0.05 Å. The angles formed by the NO<sub>2</sub> groups with the square coordination plane are listed in Table 6, compared with the geometry of some tetranitropalladates(II). In all structures containing the  $[Pd(NO_2)_4]^{2-}$ complex anion, the square coordination of Pd is transformed to an extended bipyramid due to Pd···O(NO<sub>2</sub>) contacts. In compound I the square-planar coordination of the Pd atom is transformed to (4 + 1 + 1) due to two nitro oxygen atoms from neighboring complex anions, with Pd…O distances of 3.003 and 3.184 Å. Zigzag chains of complex anions with a Pd…Pd distance of 4.884 Å and a PdPdPd angle of 106.9° running along axis z are formed due to such contacts. A chain fragment is shown in Fig. 1. The nitro groups of the anion have the following geometry: N–O<sub>av</sub> = 1.18 Å, and  $\angle ONO_{av} = 123^{\circ}$ . It is interesting that the geometry of the nitro groups involved in the extra coordination of the palladium atom differs noticeably from the average values: the N–O bonds are shortened to 1.04 Å, the

**Table 5.** Bond lengths (*d*) and bond angles ( $\omega$ ) in the structure of **II** 

Bond	d, Å	Angle	w, deg
Pt(1)–N(4)	1.972(16)	N(12)Co(1)N(15)	88.0(8)
Pt(1) - N(2)	1.975(19)	N(16)Co(1)N(15)	89.7(7)
Pt(1) - N(1)	2.003(19)	N(13)Co(1)N(15)	178.0(6)
Pt(1)–N(3)	2.06(3)	N(12)Co(1)N(14)	179.4(7)
Pt(2)–N(8)	1.98(2)	N(16)Co(1)N(14)	90.8(6)
Pt(2)–N(5)	2.02(2)	N(13)Co(1)N(14)	88.9(6)
Pt(2)–N(6)	2.04(2)	N(15)Co(1)N(14)	92.6(6)
Pt(2)–N(7)	2.05(2)	N(12)Co(1)N(11)	90.2(7)
Co(1)–N(12)	1.912(19)	N(16)Co(1)N(11)	179.7(7)
Co(1)–N(16)	1.913(15)	N(13)Co(1)N(11)	91.0(7)
Co(1)–N(13)	1.952(15)	N(15)Co(1)N(11)	90.4(7)
Co(1)–N(15)	1.953(17)	N(14)Co(1)N(11)	89.5(6)
Co(1)–N(14)	1.958(11)	N(26)Co(2)N(23)	88.9(7)
Co(1)–N(11)	1.976(14)	N(26)Co(2)N(25)	89.5(7)
Co(2)–N(26)	1.927(16)	N(23)Co(2)N(25)	88.7(7)
Co(2)–N(23)	1.936(16)	N(26)Co(2)N(24)	89.3(7)
Co(2)–N(25)	1.948(16)	N(23)Co(2)N(24)	92.1(7)
Co(2)–N(24)	1.950(17)	N(25)Co(2)N(24)	178.5(6)
Co(2)–N(22)	1.987(11)	N(26)Co(2)N(22)	88.9(6)
Co(2)–N(21)	2.014(15)	N(23)Co(2)N(22)	177.7(6)
N(16)–O(16A)	1.20(2)	N(25)Co(2)N(22)	90.8(7)
N(16)–O(16B)	1.26(2)	N(24)Co(2)N(22)	88.4(7)
N(26)–O(26B)	1.21(2)	N(26)Co(2)N(21)	177.7(7)
N(26)–O(26A)	1.29(2)	N(23)Co(2)N(21)	88.8(7)
N(1)–O(11)	1.13(2)	N(25)Co(2)N(21)	89.9(7)
N(1)–O(12)	1.27(2)	N(24)Co(2)N(21)	91.3(7)
N(2)–O(22)	1.27(2)	N(22)Co(2)N(21)	93.4(6)
N(2)–O(21)	1.28(2)	O(16A)N(16)O(16B)	120.4(15)
N(3)–O(31)	1.13(3)	O(16A)N(16)Co(1)	120.7(12)
N(3)–O(32)	1.21(2)	O(16B)N(16)Co(1)	118.7(14)
N(4)–O(42)	1.13(2)	O(26B)N(26)O(26A)	122.1(15)
N(4) - O(41)	1.28(2)	O(26B)N(26)Co(2)	120.8(13)
N(5)–O(51)	1.19(2)	O(26A)N(26)Co(2)	117.1(14)
N(5)–O(52)	1.32(2)	O(11)N(1)O(12)	118.5(19)
N(6)–O(61)	1.16(2)	O(11)N(1)Pt(1)	122.8(16)
N(6)–O(62)	1.17(2)	O(12)N(1)Pt(1)	118.5(13)
N(7)–O(72)	1.07(2)	O(22)N(2)O(21)	114.5(19)
N(7)–O(71)	1.22(2)	O(22)N(2)Pt(1)	120.8(13)
N(8)–O(82)	1.04(3)	O(21)N(2)Pt(1)	124.6(15)
N(8)–O(81)	1.48(2)	O(31)N(3)O(32)	119(3)
A _ 1	1	O(31)N(3)Pt(1)	120.1(19)
Angle	(0, deg	0(32)N(3)Pt(1)	112.7(15)
N(4)Pt(1)N(2)	90.7(8)	O(42)N(4)O(41)	112.3(18)
N(4)Pt(1)N(1)	1/5.0(11)	O(42)N(4)Pt(1)	126.0(16)
N(2)Pt(1)N(1)	93.4(8)	O(41)N(4)Pt(1)	121.1(16)
N(4)Pl(1)N(5) N(2)Pt(1)N(2)	87.9(9)	O(51)N(5)O(52)	119.0(19)
N(2)Pt(1)N(3)	1/8.1(7)	O(51)N(5)Pt(2)	116.0(17)
N(1)P((1)N(3) N(2)D(2)N(5)	88.1(9) 00.1(9)	O(52)N(5)Pt(2)	121.9(15)
$\frac{1}{2} \frac{1}{2} \frac{1}$	90.1(8) 170.2(9)	O(01) IN(0) O(02) O(61) N(6) Pt(2)	120(2) 115 9(14)
N(0)F(2)N(0) N(5)Dt(2)N(6)	1/9.3(8)	O(01)IN(0)Pl(2) $O(62)N(6)P(2)$	113.ð(14) 119 5(14)
$\frac{1}{3} \frac{1}{1} \frac{1}$	07.3(8) 05.1(0)	O(02) N(0) P(2) O(72) N(7) O(71)	110.3(14)
N(0)P((2)N(7) N(5)P(2)N(7)	93.1(9) 172 6(10)	O(72)N(7)O(71) O(72)N(7)P(2)	$\frac{11}{(2)}$ 124 0(17)
IN(J)F((2)IN(7)) N(6)D(7)	1/3.0(10) 85.2(0)	O(72)N(7)P(2) O(71)N(7)P(2)	124.9(17) 117.5(16)
N(0)P((2)N(7)) N(12)Co(1)N(16)	63.2(9) 80.5(7)	O(71)N(7)P(2) O(82)N(8)O(81)	117.3(10) 106(2)
N(12)CO(1)N(10) N(12)Co(1)N(12)	07.J( <i>1</i> ) 00.5(8)	O(02)IN(0)O(01) O(82)N(8)D(2)	100(2) 127(2)
N(12)CO(1)N(13) N(16)Co(1)N(12)	90.J(8) 88.0(7)	O(02)IN(0)F(12) O(81)N(8)Pt(2)	137(2) 112 7(10)
11(10)C0(1)I1(13)	00.9(7)	O(01)IN(0)II(2)	113.7(10)

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Table 6. Comparative geometry of  $[M(NO_2)_4]^{2-}$  anions in the structures of salts according to [10] and this work\*

Complex	Pd–N, Å NPdN, deg <i>n</i>	N–O, Å	ONO, deg φ, deg	Pd…O, Å
$\overline{\text{Li}_2[\text{Pd}(\text{NO}_2)_4] \cdot 2\text{H}_2\text{O}}$	2.029–2.037	1.197–2.240	118–122	3.10
	88.44, 91.56		56 (×2), 48, 73	
	1			
$Na_2[Pd(NO_2)_4]$	2.015-2.053	1.190–1.261	118–121	2.90
	87.5–91.8		32, 70	
	1			
$K_2[Pd(NO_2)_4]$	2.013-2.047	1.226-1.239	119–119	3.25 Ë 3.28
	88		43, 54, 69, 88	
	2			
$\beta$ -Rb <sub>2</sub> [Pd(NO <sub>2</sub> ) <sub>4</sub> ]	2.019, 2.038	1.211-1.247	118, 119	3.09
	89, 29		82, 28	
	1			
$\alpha$ -Cs <sub>2</sub> [Pd(NO <sub>2</sub> ) <sub>4</sub> ]	1.980-2.120	0.98–1.29	108–128	_
	87		6, 88	
	3			
$[Co(NH_3)_5NO_2][Pd(NO_2)_4]$	2.025-2.173	1.040-1.236	118–134	3.10
	89.8–90.0		59, 63, 53, 38	
	1			
Complex	Pt–N, Å NPtN, deg <i>n</i>	N–O, Å	ONO, deg $pt \cdots O$ , $pt \phi$ , deg $pt \cdots N$ , $pt $	
K <sub>2</sub> [Pt(NO <sub>2</sub> ) <sub>4</sub> ]	2.030-2.047	1.197–1.252	120	-
	88		49, 86 (×2), 40, 67, 71	
	2			
$[\text{Co}(\text{NH}_3)_5\text{NO}_2][\text{Pt}(\text{NO}_2)_4] \cdot 1.5\text{H}_2\text{O}$	1.972-2.050	1.04–1.48	106–120	3.405
	88–93		62, 69, 66, 46	3.626
	2		16, 52, 70, 74	

\* *n*—number of independent  $[M(NO_2)_4]$  complex anions in the structure;  $\varphi$ —angle formed by the nitro group and the  $[M(NO_2)_4]$  square plane.

ONO angle is increased to  $134^{\circ}$ , the Pd–N(4) distance is 0.1 Å longer than the average value, and the angle formed by the plane of this ligand with the PdN<sub>4</sub> coordination square is smaller than the angles formed by the other ligands.

The Co atoms in the structure of I are surrounded by an octahedral array of atoms (CoN<sub>6</sub>) formed by the five ammonia molecules and the NO<sub>2</sub> group. The Co– N(NH<sub>3</sub>) bond lengths average 1.967 Å; the Co–N(NO<sub>2</sub>) distance is 1.911 Å. The bond angles at the Co atoms deviate by  $2.4^{\circ}$  from their ideal values. The shortest Co-Co contacts in the structure are 6.530 Å; the eight shortest distances between the centers of the complex anions and complex cations fall in the range 6.287–7.970 Å.

Structural fragments are linked through weak hydrogen bonds; the minimal estimates of the N–H···O (N···O) distances are 2.89 Å. The shortest contact between the oxygen atoms  $O(CoNO_2)$ ···O(PdNO<sub>2</sub>) is 2.99 Å.



Fig. 1. Fragment of the crystal structure of I. The dashed lines show the shortest Pd…O distances (in Å).

**Crystal structure of**  $[Co(NH_3)_5NO_2][Pt(NO_2)_4]$  • **1.5H<sub>2</sub>O (compound II).** The crystal chemistry of complexes with the  $[Pt(NO_2)_4]^{2-}$  anion is less known. Crystal chemistry has been described for K<sub>2</sub>[Pt(NO<sub>2</sub>)<sub>4</sub>] [9] and Ag<sub>4</sub>A<sub>2</sub>[Pt(NO<sub>2</sub>)<sub>4</sub>]<sub>3</sub> with A = K or Rb [10].

The structure of salt II is built of isolated  $[Co(NH_3)_5NO_2]^{2+}$  complex cations,  $[Pt(NO_2)_4]^{2-}$  complex anions, and crystal water molecules (Fig. 2). There are two crystallographically independent complex cations and two crystallographically independent complex anions in the structure; the complex species are in general positions. The geometric parameters of the complex cations are the following:  $Co-N(NH_3)_{av} = 1.96 \text{ Å}$ , Co–N(NO<sub>2</sub>) = 1.92 Å, N– $O_{av}$  = 1.24 Å,  $\angle ONO_{av}$  = 121°. The shortest Co…Co distance in the structure of II is 6.020 Å. The coordination polyhedra around the Pt atoms are slightly distorted squares formed by the four nitro nitrogen atoms; the average Pt-N bond length is 2.01 Å; deviation of the NPtN angles from ideal values (90° and 180°) reaches 6.4°. The PtN<sub>4</sub> fragments are planar squares; the departure of the atoms from the coordination plane is no more than 0.03 Å. The planes of the Pt(1) and Pt(2) coordination squares are nearly parallel; the angle formed by the normals to these planes is as small as 0.3°. The geometric parameters of the  $[Pt(NO_2)_4]^{2-}$  complex anions, including the angles of the nitro groups, are listed in Table 6. The



Fig. 2. Fragment of the crystal structure of II. The dashed lines show the shortest  $Pt \cdots O$  distances (in Å).

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**Fig. 3.** Fragment of the X-ray diffraction pattern for a metal powder produced by the thermolysis of salt **II** in a mixture with ammonium chloride (1 : 10 wt/wt) at 500°C under helium after washing off cobalt chloride with water: (*1*) observed intensities, (2) platinum (a = 3.923 Å), (3) Pt<sub>0.90</sub>Co<sub>0.10</sub> solid solution (a = 3.890 Å), (4) Pt<sub>0.75</sub>Co<sub>0.25</sub> solid solution (a = 3.855 Å), and (5) Pt<sub>0.60</sub>Co<sub>0.40</sub> solid solution ( $a_3 = 3.795$  Å).

 $[Pt(NO_2)_4]^{2-}$  anions in the structure are paired with a Pt…Pt distance equal to 5.282 Å (Fig. 2). The structural units in a crystal are linked through weak hydrogen bonds N–H…O and O(W)–H…O, equal to 2.89 and 2.96 Å, respectively. The crystal water molecules are hydrogen bonded mainly with the cations.

Thermal properties. Compounds I and II decomposed in flowing helium in the same manner, with two well-defined exotherms at 160 and 230°C for compound I and at 160 and 250°C for compound II. The thermolysis of complex **II** was preceded by water loss at 90-100°C. Dehydration was achieved under isothermal conditions. Heating complex II in vacuum at 100°C for 10 h dehydrated about half of the starting amount of the salt; the salt transformed to a phase structural to compound I with the following monoclinic unit cell parameters: a = 8.01 Å, b = 22.27 Å, c = 7.93 Å,  $\beta = 99.4^{\circ}$ . Further heating at this temperature decomposed the complex; after 3 days, the complex completely transformed to a phase with an unknown structure. The IR spectrum of this phase did not differ from the spectrum of the starting compound, which proved the absence of ligand rearrangement between the cation and anion.

We characterized the final products of thermolysis of complex II under helium using X-ray powder diffraction. After the complex was heated to 500°C, a mixture of metal platinum and Co<sub>3</sub>O<sub>4</sub> was formed. Heating a mixture of complex II and ammonium chloride (1:10 wt/wt) to the same temperature produced cobalt(II) chloride and a polyphase metal mixture. Figure 3 shows the X-ray diffraction pattern from the powder obtained after water washing of cobalt chloride. The complex profile of each diffraction peak was formed by reflections from pure platinum and the  $Pt_{1-x}Co_x$  solid-solution series based on the face-centered cubic (fcc) lattice of platinum. The figure displays an approximate model in which the reflection profile is formed by platinum (a = 3.923 Å) and three solid solutions with the parameters  $a_1 = 3.885$  Å,  $a_2 = 3.855$  Å, and  $a_3 = 3.790$  Å. The compositions of the solid solutions were estimated from the Zen rule [11] (assuming the additivity of the volume per atom in the solid solution) as follows:  $Pt_{0.90}Co_{0.10}$ ,  $Pt_{0.75}Co_{0.25}$ , and Pt<sub>0.60</sub>Co<sub>0.40</sub>, respectively. We may suggest that ammonium chloride reduced part of the cobalt during the



**Fig. 4.** Fragment of the X-ray diffraction pattern for a metal powder produced by the thermolysis of salt **II** under a hydrogen atmosphere at 450°C: (1) observed intensities, (2)  $Pt_{0.80}Co_{0.20}$  solid solution ( $a_1 = 3.870$  Å), and (3)  $Pt_{0.60}Co_{0.40}$  solid solution ( $a_2 = 3.805$  Å).



Fig. 5. Fragment of the X-ray diffraction pattern for a metal powder produced by the thermolysis of salt I under a hydrogen atmosphere (1) without thermal diluent and (2) with ammonium chloride used as a thermal diluent.

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thermolysis, and the metal cobalt formed solid solutions with platinum.

The thermolysis products of complex II in hydrogen were obtained in two ways. In the first case, the complex was heated to 450°C under a hydrogen atmosphere, then it was cooled under the hydrogen atmosphere. The final product was two fcc phases (Fig. 4) with the cubic unit cell parameters  $a_1 = 3.870$  Å and  $a_2 = 3.805$  Å, which corresponded to  $Pt_{0.80}Co_{0.20}$  and Pt<sub>0.60</sub>Co<sub>0.40</sub> solid solutions, respectively. The CSD sizes were 100–150 and 50–70 Å, respectively. In the second case, the heating schedule was the same but ammonium chloride was used as the thermal diluent. The X-ray diffraction pattern of the product nearly coincided, in its peak intensities and positions, with the PDF card 65-8969 for intermetallic compound CoPt. The tetragonal unit cell parameters (a = 3.794 Å, c = 3.724 Å) slightly differed from the standard values.

The thermolysis products of salt **I** in flowing hydrogen were studied in the same manner. The final product was a single-phase sample with the fcc unit cell parameter a = 3.750 Å (CSD sizes were 100–150 Å), which corresponded to a solid solution with an approximate composition of Pd<sub>0.45</sub>Co<sub>0.55</sub>. Heating in the presence of a thermal diluent (ammonium chloride) yielded a solid solution with the parameter a = 3.785 Å and the composition Pd<sub>0.50</sub>Co<sub>0.50</sub>. The sample also contained less than 2 wt % of metal palladium (Fig. 5).

Proceeding from the data above, we may infer that the metal products of thermolysis of compounds I and II are strongly affected by the process parameters. By varying the temperature and gas ambiance, one can determine the phase composition of the products and the dispersivity of the resulting powders.

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