Synthesis, structure, and thermal transformations of double complex salts $[Au(C_4H_{13}N_3)Cl][MCl_6] \cdot nH_2O$ (M = Ir, Pt; n = 0—2)

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Double complex salts $[Au(C_4H_{13}N_3)Cl][MCl_6] \cdot nH_2O$ (M = Ir, Pt; n = 0—2) were synthesized. According to X-ray diffraction data, compounds with n = 1.5 are isostructural; the crystal structure is composed of the complex cations $[Au(dien)Cl]^{2+}$ (dien is diethylenetriamine), the complex anions $[MCl_6]^{2-}$, and water molecules of crystallization. Thermolysis of the double complex salts under hydrogen and helium was studied. The formation of nonequilibrium solid solutions based on Ir in the Au—Ir system and based on Pt in the Au—Pt system was demonstrated.

Key words: gold, iridium, platinum, double complex salts, diethylenetriamine, X-ray diffraction, thermal analysis, solid solutions.

A large number of double complex salts (DCS) have now been synthesized. These salts are used as precursors of bi- and polymetallic powders, which are produced by thermal decomposition of these salts.[1,2] The considerable interest in these compounds is, first of all, due to the fact that they can be used to prepare highly effective heterogeneous catalysts.[3,4] Gold-containing systems have remained so far beyond the scope of studies along this line, although gold-containing catalysts have been tested rather vigorously in recent years, for example, for low-temperature CO oxidation.[5—7]

The purpose of this work is to synthesize and study double complex salts containing gold(III), iridium(IV), and platinum(IV) and to investigate the metallic phases formed on their thermal decomposition.

Results and Discussion

Usually double complex salts containing a complex cation of one metal and a complex anion of another metal are prepared by mixing aqueous solutions containing these complex ions.[1,2] The polycrystalline DCS samples $[Au(dien)Cl][IrCl_6] \cdot nH_2O$, n = 0.8—1.2 (**1**) and $[Au(dien)Cl][PtCl_6] \cdot nH_2O$, n = 0.6—1.1 (**2**) (dien is diethylenetriamine) were prepared in this way under controlled conditions in the reaction solution. The initial complex $[Au(dien)Cl]Cl_2$ is a weak acid[8] (pK_a = 4.0); therefore, to eliminate the formation of DCS with the conjugate base $[Au(dien^*)Cl]^+$, where (dien*) is the deprotonated diethylenetriamine molecule, compounds **1** and **2** were prepared at pH ≤ 2. The maintenance of the relation pH + pCl ≤ 5.2 in the reaction solution excludes the formation of the products of hydrolysis of gold(III) complex. Moreover, high concentrations of H^+ and Cl^- in the solution are undesirable because of instability of $Au(dien)Cl^{2+}$ through replacement of the dien molecules by chloride ions to give $AuCl_4^-$ and $dienH_3^{3+}$. The electronic absorption spectra of solutions of **1** and **2** in 0.02 *M* $HClO_4$ recorded immediately after solution preparation are superpositions of the spectra of the starting compounds $[Au(dien)Cl]Cl_2$ and $Na_2[MCl_6]$ (M = Ir^{IV}, Pt^{IV}) in the same solvent. Thus, the inner coordination sphere of the starting complex ions remains unchanged in the DCS.

The presence of water in DCS **1** and **2** is confirmed by the IR spectra and by the weight loss upon thermolysis. The variable content of water and the ease of its removal during thermolysis indicates that this is water of crystallization. Note that the powder X-ray diffraction patterns of these compounds containing different amounts of water are identical.

Good-quality single crystals were obtained only for n = 1.0 and 1.5 for Ir^{IV} and n = 1.5 for Pt^{IV}.

Previously, we found[2] that, depending on the synthesis temperature, the amount of water in some DCS can vary. In our case, a decrease in the synthesis temperature to 0 °C resulted in DCS containing two water molecules, $[Au(dien)Cl][IrCl_6] \cdot 2H_2O$. The water content was determined by TG. Powder X-ray diffraction analysis of this salt showed that its structure differed from the structures of compounds with fewer water molecules. We were unable to grow a single crystal of this compound.

The IR spectra of the DCS exhibit a broad band at 3500—3200 cm^{-1}, unlike the IR spectrum of the complex

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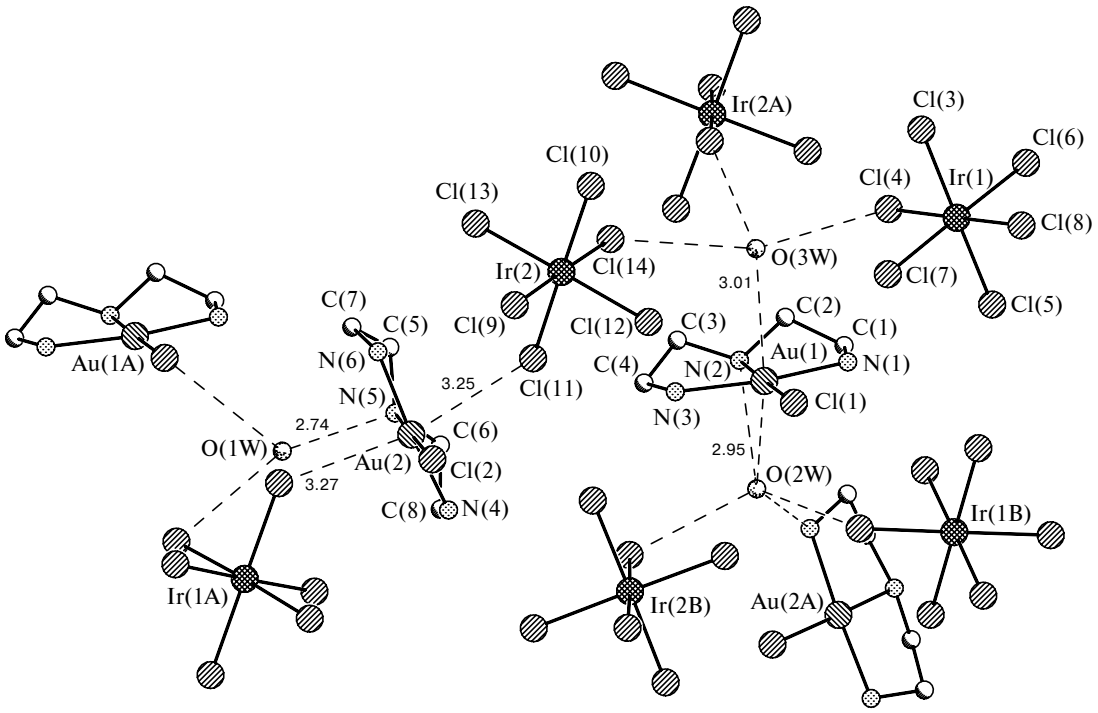

Fig. 1. Fragment of the crystal structure of $[Au(dien)Cl][IrCl_6] \cdot 1.5H_2O$.

$[Au(dien)Cl]Cl_2$, with a fine structure, indicative of the presence of intramolecular hydrogen bonds.

The structures of $[Au(dien)Cl][MCl_6] \cdot 1.5H_2O$ (M = Ir, Pt). The compounds $[Au(dien)Cl][IrCl_6] \cdot 1.5H_2O$ and $[Au(dien)Cl][PtCl_6] \cdot 1.5H_2O$ are isostructural; therefore, the crystal structure will be given for the iridium-containing compound. The structure is composed of the $[Au(dien)Cl]^{2+}$ cations, the $[IrCl_6]^{2-}$ anions, and water molecules of crystallization (Fig. 1). The two crystallographically independent $[Au(dien)Cl]^{2+}$ cations have no symmetry elements; the gold atoms occupy general positions. The gold coordination polyhedron is a distorted square formed by three nitrogen atoms of the dien molecule and the chlorine atom. The Au—N bond lengths are in a range of 2.005—2.044 Å (the average is 2.034), the Au—Cl_{aver} length is 2.275 Å, and the bond angles deviate from 90° by at most 6.3°. The square coordination of Au(2) is completed to a (4+2) elongated bipyramid by two chlorine atoms from two different $[IrCl_6]^{2-}$ anions; the corresponding Au(2)...Cl distances are 3.25 and 3.27 Å, which is smaller than the sum of the van der Waals radii of Au and Cl (3.8 Å).[9] The axial positions nearest to Au(1) are occupied by water molecules at Au...O distances of 3.01 and 3.42 Å. The geometric characteristics of the gold complex cations are comparable with those reported in the literature, for example, for the compound $[Au(dien)Cl]Cl(ClO_4)$ (see Ref. 10).

In the octahedral $[IrCl_6]^{2-}$ anions, the Ir—Cl distances are in the 2.295—2.338 Å range, the average value of 2.317 Å being in good agreement with the published data[11] for compounds incorporating $[IrCl_6]^{2-}$ anions, for example, for the double complex salts $[Ir(NH_3)_5Cl]_2[MCl_6]Cl_2$, where M = Ir, Pt. The Cl...Cl contacts between the complex anions are 3.21—3.45 Å. The complex cations arranged between the complex anions form hydrogen bonds with the chlorine atoms of the neighboring anionic complexes and with water molecules (Fig. 2).

The structure contains three crystallographically independent water molecules of crystallization with different structural functions. The O(1W) molecule forms a hydrogen bond with the H atom of the secondary amino group of the Au(2) complex, the O...N distance is 2.74 Å. The Cl atoms of complex ions are involved in the O(1W)...Cl contacts equal to 3.46 Å. The O(2W) molecule forms a hydrogen bond with the H atom of the secondary amino group of the Au(1) complex, thus completing the Au(1) coordination (the O...N distance is 2.95 Å). The shortest O(2W)...Cl contacts with the Cl atoms of the complex anions are 3.19 and 3.38 Å. The O(3W) atom completes the Au(1) coordination, the Au...O distance being 3.01 Å and contacts with chlorine atoms being 3.25—3.36 Å.

The compound $[Au(dien)Cl][IrCl_6] \cdot H_2O$ is isostructural to the above-described salts with the only difference that the position occupied by the O(3W) water molecule remains vacant.

Thermal transformations of compounds **1** and **2** are generally the same. The thermogram of compound **1** recorded in a helium atmosphere at a heating rate

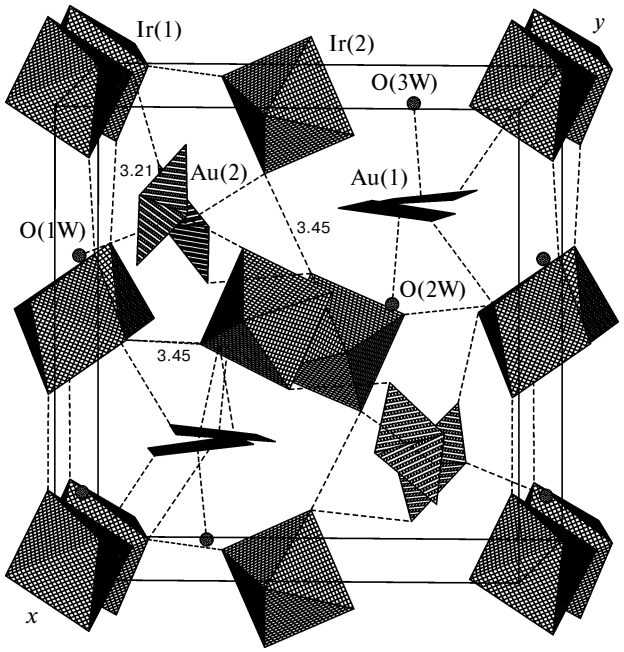

Fig. 2. General view of the crystal structure of $[Au(dien)Cl][IrCl_6] \cdot 1.5H_2O$.

of 10 °C·min^{-1} is shown in Fig. 3. Compound decomposes in several stages. The first one occurs in the temperature range of 80—120 °C and is accompanied by a slight endotherm and a weight loss corresponding to the removal of the water of crystallization. The subsequent decomposition takes place in the temperature range of 180—725 °C and is accompanied by the loss of another ~41% of the weight. The initial stage of the decomposition in the 180—220 °C range is accompanied by a pronounced exotherm. The overall weight loss is 43.5%. According to powder X-ray diffraction, the thermolysis product represents two metallic phases whose reflections strictly correspond to the phases of pure gold and pure iridium. The higher weight of the thermolysis product compared to the total weight of metals is due to incomplete removal of carbon under these conditions. The presence of carbon in the products is confirmed by laser pulse mass spectrometry.

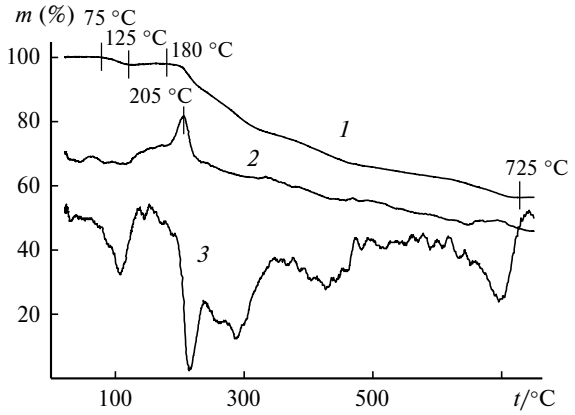

Fig. 3. Thermogravimetric pattern of DCS **1** in a helium atmosphere. Heating rate ~10 °C/min.: (*1*) TG, (*2*) DTA, (*3*) DTG.

The reduction in a hydrogen atmosphere proceeds at lower temperatures (400 °C) and also gives rise to a two-phase system. A fragment of the X-ray diffraction pattern of the product of DCS **1** reduction under hydrogen at 250 °C is shown in Fig. 4. The X-ray diffraction pattern is formed by two sets of reflections corresponding to phases with face-centered cubic lattices characterized by cell parameters $a_1 = 4.078(1)$ Å and $a_2 = 3.874(3)$ Å. The narrow peaks belong to the pure gold phase[12] ($a_{Au} = 4.0786$ Å). The smaller parameter corresponds to the solid solution phase $Au_{0.15}Ir_{0.85}$, whose composition was estimated by Vegard´s rule. Analysis of reflection profile broadening gives an average crystallite size (CZ) of 120—200 Å for the gold phase and 30—40 Å for the solid solution phase. According to the phase diagram,[13] gold and iridium are have limited mutual solubility in the liquid state. The highest solubility of iridium in gold in the solid state is 0.1 at.%, and the solubility of gold in iridium is at most 2 at.%. Hence, it follows that the resulting solid solution $Au_{0.15}Ir_{0.85}$ is nonequilibrium.

The reduction of DCS **2** in a hydrogen atmosphere also furnishes a powder containing two metallic phases. More precise determination of the unit cell parameters for these phases gives $a_1 = 4.078(1)$ Å and $a_2 = 3.935(3)$ Å, which correspond to pure metallic gold and a substitution solid solution based on platinum $Au_{0.10}Pt_{0.90}$. The size of crystallites is 90—150 Å for the gold phase and 70—90 Å for the solid solution phase. The equilibrium solubility of gold in platinum at 600 °C does not exceed 3 at.% and decreases on lowering the temperature.[13] Thus, the solid solution phase of the given composition formed upon the reduction at 400 °C is also nonequilibrium.

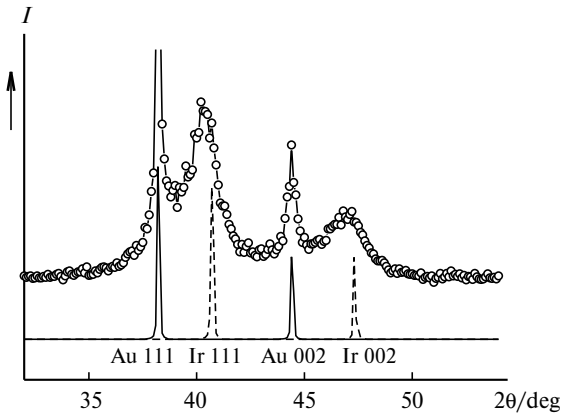

Fig. 4. Fragment of the experimental X-ray diffraction pattern (reflections 111, 002) of the metallic powder obtained by thermolysis of DCS **1**; dots are experimental values; continuous line is the theoretical X-ray diffraction pattern of gold; and dashed line is the theoretical X-ray diffraction pattern of iridium.

In view of the above-noted variability of the composition of compounds as regards the number of water molecules, additional experiments were carried out. For this purpose, samples of DCS **1** were heated in air to 130 °C and then cooled for 3—5 min and weighed. Then the dehydrated sample ($n = 0$) was kept in air at room temperature; this was accompanied by an increase in the sample weight. A constant weight was attained in 20—24 h. Three or four cycles were carried out in this way until a constant weight loss and a constant weight gain were attained. The weight loss in the first cycle was found to be always greater than that in the subsequent cycles. Irrespective of the number of water molecules present initially in DCS (2 to 0.8), the final product contained ~0.8 water molecules and, according to powder X-ray diffraction, this was a single phase with parameters corresponding to the DCS $[Au(dien)Cl][IrCl_6] \cdot H_2O$. This behavior of water molecules is apparently related to different types of their interaction with structure fragments.

Thus, we report the first synthesis of double complex salts containing Au^{III} complex cations and Ir^{IV} or Pt^{IV} complex anions and determination of their crystal structures. The possibility of preparing metastable solid solutions $Au_{0.15}Ir_{0.85}$ and $Au_{0.10}Pt_{0.90}$ is demonstrated.

Experimental

Electronic absorption spectra were measured in the 50000—14000 cm^{-1} on a SPECORD UV VIS spectrophotomer. The IR spectra of the polycrystalline samples as mineral and fluorinated oil mulls were recorded on a Specord IR-75 instrument in the region of 3800—400 cm^{-1}. Mass spectrometric studies were carried out on an EMAL-2 mass analyzer with a laser ion source.

Table 1. Crystal data and X-ray experiment parameters for compounds $[Au(dien)Cl][IrCl_6] \cdot 1.5H_2O$ (**1**), $[Au(dien)Cl][PtCl_6] \cdot 1.5H_2O$ (**2**), and $[Au(dien)Cl][IrCl_6] \cdot H_2O$ (**3**)

Parameter	**1**	**2**	**3**
Molecular formula	$Au_2Cl_{14}C_8H_{32}Ir_2N_6O_3$	$Au_2Cl_{14}C_8H_{32}N_6O_3Pt_2$	$Au_2Cl_{14}C_8H_{30}Ir_2N_6O_2$
M	1535.12	1540.82	1577.08
T/K	293(2)	273(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
System	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$	$Pca2_1$
Unit cell parameters			
a/Å	14.798(3)	14.7873(5)	14.7644(5)
b/Å	14.538(3)	14.5490(5)	14.4869(5)
c/Å	15.499(3)	15.4997(4)	15.4893(4)
V/Å^3	3334.2(12)	3334.61(18)	3313.01(18)
Z	4	4	4
d_{calc}/g cm^{-3}	3.046	3.057	3.033
μ/mm^{-1}	17.877	18.283	17.988
F(000)	2760	2768	2728
Data collection range over θ/deg	1.40—32.42	1.40—35.86	1.41—26.38
Range of h, k, l	$-13 \le h \le 21$	$-24 \le h \le 22$	$-18 \le h \le 18$
	$-21 \le k \le 21$	$-23 \le k \le 23$	$-18 \le k \le 18$
	$-12 \le l \le 19$	$-24 \le l \le 11$	$-18 \le l \le 12$
The number of measured reflections	18085	33650	23966
The number of independent reflections	8090	9669	5371
Completeness of data collection over θ° (%)	32.42 (81.6)	35.86 (92.0)	26.38 (98.5)
The number of reflections	8090	9669	5371
The number of constraints	1	1	1
The number of parameters	330	330	308
S-factor on F^2	1.086	1.071	1.009
R-factor ($I > 2\sigma(I)$)			
R_1	0.0371	0.0391	0.0299
wR_2	0.0911	0.1133	0.0498
R-factor (all data)			
R_1	0.0491	0.0467	0.0462
wR_2	0.0956	0.1182	0.0528
Residual electron density (max/min)/e A^{-3}	2.135/−0.858	3.042/−1.025	1.413/−0.913

Elemental analysis was carried out at the Novosibirsk Institute of Organic Chemistry, Siberian Branch of the RAS, on a Carlo—Erba automatic analyzer. The sum of metals in DCS **1** and **2** was carried out by reduction of DCS in an H_2 flow at 400 °C; after that, the resulting metallic powder was kept for 20 min in a helium flow at 600 °C, cooled, and weighed.

Thermogravimetric measurements were carried out on a Q1000 derivatograph modified for experiments in the atmosphere of different gases (air, helium). A sample (~100 mg) was placed in a quartz crucible with a lid and heated at a 10 °C min^{-1} rate in a helium flow (150 mL min^{-1}) or in air.

X-Ray diffraction analysis was carried out at room temperature on a Bruker-Nonius X8Apex four-circle automated diffractometer equipped with an *xy*-detector (Mo*K*α radiation, graphite monochromator). The crystal data for the compounds under study and X-ray experiment details are presented in Table 1. The structures were solved by the standard heavy-atom method and refined in the anisotropic-isotropic (for H) approximation, and the hydrogen atoms were specified geometrically. The principal interatomic distances and bond angles of the complexes are summarized in Table 2. All calculations were carried out by the SHELX-97 program package.[14]

Powder X-ray diffractions were obtained on a DRON-SEIFERT-RM4 diffractometer (Cu-Kα radiation, reflected beam graphite monochromator, scintillation detector with amplitude discrimination). The samples were prepared by application of an alcohol suspension on a polished side of a standard quartz cell. A polycrystalline silicon sample prepared in a similar way was used as the reference (a = 5.4309 Å). The X-ray diffraction patterns of the complex salts were recorded in a stepwise mode in the $5° \le 2\theta \le 60°$ range; those for thermolysis products, in the $5° \le 2\theta \le 135°$ range.

The X-ray diffraction patterns of the thermolysis products were recorded using the data for pure metals and compounds given in the PDF card file.[12] The metallic phase parameters

Table 2. Selected interatomic distances (d) and bond angles (ω) in the structures [Au(dien)Cl][$IrCl_6$]·1.5H_2O (**1**) and [Au(dien)Cl][$PtCl_6$]·1.5H_2O (**2**)

1				**2**			
Distance	d/Å	Angle	ω/deg	Distance	d/Å	Angle	ω/deg
Ir(1)—Cl(5)	2.304(3)	Cl(5)—Ir(1)—Cl(6)	90.12(13)	Pt(1)—Cl(5)	2.312(3)	Cl(5)—Pt(1)—Cl(6)	88.69(13)
Ir(1)—Cl(6)	2.316(3)	Cl(5)—Ir(1)—Cl(4)	89.37(13)	Pt(1)—Cl(6)	2.362(3)	Cl(5)—Pt(1)—Cl(4)	88.12(12)
Ir(1)—Cl(3)	2.320(3)	Cl(3)—Ir(1)—Cl(4)	90.25(13)	Pt(1)—Cl(3)	2.308(3)	Cl(3)—Pt(1)—Cl(4)	89.97(13)
Ir(1)—Cl(7)	2.320(3)	Cl(7)—Ir(1)—Cl(4)	89.51(14)	Pt(1)—Cl(7)	2.272(3)	Cl(7)—Pt(1)—Cl(4)	89.69(15)
Ir(1)—Cl(4)	2.322(3)	Cl(7)—Ir(1)—Cl(8)	88.73(16)	Pt(1)—Cl(4)	2.353(3)	Cl(7)—Pt(1)—Cl(8)	90.77(16)
Ir(1)—Cl(8)	2.323(4)	Cl(9)—Ir(2)—Cl(10)	89.37(16)	Pt(1)—Cl(8)	2.286(4)	Cl(9)—Pt(2)—Cl(10)	91.14(18)
Ir(2)—Cl(13)	2.295(3)	Cl(9)—Ir(2)—Cl(12)	89.89(16)	Pt(2)—Cl(13)	2.316(3)	Cl(9)—Pt(2)—Cl(12)	91.84(19)
Ir(2)—Cl(14)	2.307(4)	Cl(10)—Ir(2)—Cl(12)	91.70(12)	Pt(2)—Cl(14)	2.360(4)	Cl(10)—Pt(2)—Cl(12)	92.47(11)
Ir(2)—Cl(11)	2.315(3)	Cl(11)—Ir(2)—Cl(12)	87.50(12)	Pt(2)—Cl(11)	2.316(3)	Cl(11)—Pt(2)—Cl(12)	87.48(12)
Ir(2)—Cl(9)	2.319(4)	Cl(13)—Ir(2)—Cl(14)	91.24(17)	Pt(2)—Cl(9)	2.267(4)	Cl(13)—Pt(2)—Cl(14)	89.59(18)
Ir(2)—Cl(10)	2.329(3)	N(1)—Au(1)—N(2)	85.6(4)	Pt(2)—Cl(10)	2.315(3)	N(1)—Au(1)—N(2)	82.8(4)
Ir(2)—Cl(12)	2.338(3)	N(1)—Au(1)—Cl(1)	93.2(3)	Pt(2)—Cl(12)	2.316(3)	N(1)—Au(1)—Cl(1)	94.0(4)
Au(1)—N(1)	2.014(10)	N(2)—Au(1)—Cl(1)	178.7(3)	Au(1)—N(1)	2.067(11)	N(2)—Au(1)—Cl(1)	176.6(3)
Au(1)—N(2)	2.022(10)	N(3)—Au(1)—Cl(1)	96.3(3)	Au(1)—N(2)	2.071(9)	N(3)—Au(1)—Cl(1)	98.6(4)
Au(1)—N(3)	2.036(11)	N(2)—Au(1)—N(3)	84.9(2)	Au(1)—N(3)	1.991(11)	N(2)—Au(1)—N(3)	84.5(2)
Au(1)—Cl(1)	2.260(4)	N(1)—Au(1)—N(3)	169.9(2)	Au(1)—Cl(1)	2.214(4)	N(1)—Au(1)—N(3)	166.6(2)
Au(2)—N(5)	2.005(10)	N(4)—Au(2)—Cl(2)	94.0(3)	Au(2)—N(5)	2.074(10)	N(4)—Au(2)—Cl(2)	95.8(3)
Au(2)—N(4)	2.035(10)	N(5)—Au(2)—Cl(2)	178.5(3)	Au(2)—N(4)	2.046(11)	N(5)—Au(2)—Cl(2)	177.6(3)
Au(2)—N(6)	2.044(10)	N(6)—Au(2)—Cl(2)	95.6(3)	Au(2)—N(6)	2.041(11)	N(6)—Au(2)—Cl(2)	97.2(4)
Au(2)—Cl(2)	2.290(4)	N(4)—Au(2)—N(5)	85.1(2)	Au(2)—Cl(2)	2.233(4)	N(4)—Au(2)—N(5)	83.2(2)
N(1)—C(1)	1.487(19)	N(6)—Au(2)—N(5)	85.2(2)	N(1)—C(1)	1.482(19)	N(6)—Au(2)—N(5)	83.5(2)
N(2)—C(3)	1.465(15)	N(4)—Au(2)—N(6)	169.2(2)	N(2)—C(3)	1.500(16)	N(4)—Au(2)—N(6)	165.1(2)
N(2)—C(2)	1.470(14)	C(1)—N(1)—Au(1)	107.2(7)	N(2)—C(2)	1.502(16)	C(1)—N(1)—Au(1)	108.8(8)
N(3)—C(4)	1.503(17)	C(3)—N(2)—C(2)	118.5(10)	N(3)—C(4)	1.51(2)	C(3)—N(2)—C(2)	119.0(10)
N(4)—C(8)	1.497(17)	C(3)—N(2)—Au(1)	106.3(8)	N(4)—C(6)	1.495(17)	C(3)—N(2)—Au(1)	106.6(7)
N(5)—C(6)	1.492(16)	C(2)—N(2)—Au(1)	103.0(7)	N(5)—C(5)	1.503(16)	C(2)—N(2)—Au(1)	106.2(7)
N(5)—C(5)	1.484(16)	C(4)—N(3)—Au(1)	107.2(8)	N(5)—C(8)	1.494(15)	C(4)—N(3)—Au(1)	109.6(8)
N(6)—C(7)	1.556(17)	C(8)—N(4)—Au(2)	108.1(8)	N(6)—C(7)	1.548(17)	C(6)—N(4)—Au(2)	110.1(8)
C(1)—C(2)	1.485(16)	C(5)—N(5)—C(6)	118.5(10)	C(1)—C(2)	1.502(18)	C(5)—N(5)—C(8)	119.1(10)
C(3)—C(4)	1.468(19)	C(6)—N(5)—Au(2)	106.7(8)	C(3)—C(4)	1.49(2)	C(8)—N(5)—Au(2)	106.4(8)
C(5)—C(7)	1.50(2)	C(5)—N(5)—Au(2)	110.0(8)	C(5)—C(7)	1.49(2)	C(5)—N(5)—Au(2)	108.8(7)
C(6)—C(8)	1.516(19)	C(7)—N(6)—Au(2)	106.3(8)	C(6)—C(8)	1.506(18)	C(7)—N(6)—Au(2)	109.0(8)
		C(3)—C(4)—N(3)	110.0(10)			C(3)—C(4)—N(3)	109.5(11)
		C(5)—C(7)—N(6)	109.7(10)			C(5)—C(7)—N(6)	108.2(10)

were refined by the least-squares method for the whole data array using the PCW program.[15]

The complexes $[Au(dien)Cl]Cl_2$, $Na_2[IrCl_6]\cdot 6H_2O$, and $Na_2[PtCl_6]\cdot 6H_2O$ were prepared by known procedures.[10,16—18] The complex $dienH_3[IrCl_6]NO_3$ was isolated by mixing aqueous solutions of $Na_2[IrCl_6]\cdot 6H_2O$ and $dienH_3Cl_3$ in nitric acid. The solution of $Na[AuCl_4]$ was prepared by dissolving gold metal in *aqua regia* followed by evaporation with concentrated HCl repeated three times and addition of the calculated amount of NaOH. "Chemically pure" grade chemicals were used as received; "pure" grade $NaClO_4$ was recrystallized from a water-ethanol mixture.

Chlorodiethylenetriaminegold(III) hexachloroiridate(IV) hydrate $[Au(dien)Cl][IrCl_6]\cdot nH_2O$, n = 0.8—1.2 (1). A cooled solution (1 mL) containing $[Au(dien)Cl]Cl_2$ (0.2 mmol) in 0.01 *M* HCl was added with stirring to a cooled solution (1 mL) containing $Na_2[IrCl_6]\cdot 6H_2O$ (0.2 mmol) in 0.02 *M* $HClO_4$. The synthesis temperature was ~10 °C. The resulting dark-cherry precipitate was filtered off under vacuum, washed on a glass filter successively with minimum amounts of cooled 0.01 *M* HCl, ethanol, and ether, and dried in air to give 0.130 g of a product, yield ~85%. Found (%): C, 6.5; H, 1.7; N, 5.7; (Au+Ir), 51.6. $C_4H_{15}Cl_7N_3OAuIr$. Calculated (%): C, 6.33; H, 1.99; N, 5.54; (Au+Ir), 51.31. The same product was obtained when the starting complexes were taken in 1 : 2 molar ratio. The water content for the given polycrystalline sample was determined by thermogravimetric analysis to be 2.3%, which corresponds to $n = 1$.

The single crystals of $[Au(dien)Cl][IrCl_6]\cdot H_2O$ suitable for X-ray diffraction were grown by crystallization of the DCS for 20 h at room temperature from a solution containing $Na[AuCl_4]$ (0.0350 mol L^{-1}), $dienH_3[IrCl_6]NO_3$ (0.0175 mol L^{-1}), and $NaClO_4$ and HCl (1.0 and 0.01 mol L^{-1}, respectively). The slow formation of the $[Au(dien)Cl]^{2+}$ cation from $[AuCl_4]^-$ and $dienH_3^{3+}$ is accompanied by growth of the DCS crystals. The resulting crystals were filtered off, washed on the filter with minimum amounts of 0.01 *M* HCl, ethanol, and ether, and dried in air. Of the crystals formed, one was selected for the X-ray diffraction experiment.

The $[Au(dien)Cl][IrCl_6]\cdot 1.5H_2O$ single crystals were obtained by slow evaporation for several days at ~5 °C of a solution containing 0.01 *M* DCS (**1**), 2.0 *M* $NaClO_4$, and 0.01 *M* HCl. The crystals were stored under the solution.

Chlorodiethylenetriaminegold(III) hexachloroplatinate(IV) hydrate, $[Au(dien)Cl][PtCl_6]\cdot nH_2O$, n = 0.6—1.1 (2). The compound was prepared similarly to **1**. The yield of the yellow product was 0.132 g (~85%). Found (%): C, 6.4; H, 2.0; N, 5.7; (Au+Pt), 52.2. $C_4H_{15}Cl_7N_3OAuPt$. Calculated (%): C, 6.31; H, 1.99; N, 5.52; (Au+Pt), 51.49. The water content for the given polycrystalline sample was determined by thermogravimetric analysis to be 1.6%, which corresponds to $n = 0.7$.

The single crystals of $[Au(dien)Cl][PtCl_6]\cdot 1.5H_2O$ suitable for X-ray diffraction were grown and were stored under a solution as in the case of M = Ir.

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