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Crystal Structures of *trans*−Diiodidobis(2−hydroxyethylamine) platinum(II) and *trans*−Dichloridobis(2,2′−dihydroxydiethylamine) platinum(II)

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*The crystal structures of trans-diiodidobis(2-hydroxyethylamine)platinum(II), trans-[$PtI_2(mea)_2$], (**1**) and trans-dichloridobis(2,2'-dihydroxydiethylamine)platinum(II), trans-[$PtCl_2(dea)_2$], (**2**) were determined by single crystal X-ray diffraction experiments. Crystallization of (**1**) occurs in the monoclinic space group $P2_1/c$ with a = 9.457(1) Å, b = 14.719(2) Å, c = 8.246(1) Å, Z = 4 for d_{calc} = 3.235 mg/m³ while crystallization of (**2**) occurs in the tetragonal space group $P4_2/mbc$, a = 9.8624(6) Å, c = 14.2998(9) Å, Z = 4 for d_{calc} = 2.274 mg/m³. The square-planar coordination geometry of both complexes is formed by two N atoms of the 2-hydroxyethylamine (**1**) or 2,2'-dihydroxydiethylamine (**2**) ligands in trans positions and two I^- (**1**) or Cl^- (2) anions. Both structures are stabilized by intra- and intermolecular hydrogen bonds.*

Keywords: Platinum(II) complexes, 2-hydroxyethylamine, 2,2'-dihydroxydiethylamine.

Кристаллические структуры *транс*—дийодидобис−(2−гидроксиэтиламина)платины(II) и *транс*—дихлоридобис−(2,2′−дигидроксидиэтиламина)платины(II)

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*С помощью рентгеноструктурного анализа были определены кристаллические структуры транс-дийодидобис(2-гидроксиэтиламина)платины(II), trans-[$PtI_2(mea)_2$], (**1**) и транс-дихлоридобис(2,2'-дигидроксидиэтиламина)платины(II), trans-[$PtCl_2(dea)_2$], (**2**). Молекула (**1**) кристаллизуется в моноклинной пространственной группе $P2_1/c$, где a = 9.457(1) Å, b = 14.719(2) Å, c = 8.246(1) Å, Z = 4 для d_{calc} = 3.235 мг/м³, молекула (**2**) – в тетрагональной пространственной группе $P4_2/mbc$, где a = 9.8624(6) Å, c = 14.2998(9) Å, Z = 4 для d_{calc} = 2.274 мг/м³. Плоскоквадратная координационная геометрия обоих комплексов образована двумя атомами азота лигандов 2-гидроксиэтиламина (**1**) или 2,2'-дигидроксидиэтиламина (**2**) в транс-положениях и двумя анионами I^- (**1**) или Cl^- (**2**). Обе структуры стабилизированы внутри- и межмолекулярными водородными связями.*

Ключевые слова: Комплексы платины(II), 2-гидроксиэтиламин, 2,2'-дигидроксидиэтиламин.

Discovery of cisplatin as cancerostatic compound and successful clinical application of it, developed widespread interest of synthesis of different platinum complexes with potential antitumor activity. The platinum(II) complexes with bis(2-hydroxyethylamine) and bis(2,2'-dihydroxydiethylamine) ligands gained great interest because of the ability of the hydroxyl groups to act as acceptors or donors for hydrogen bonds, which is expected to play an important role in the binding of platinum complexes to DNA.[1-4] The modified literature method was used for the synthesis of *trans*-diiodidobis(2-hydroxyethylamine)platinum(II) and *trans*-dichloridobis(2-hydroxyethylamine)platinum(II).[5]

Synthesis

trans-[PtI$_2$(mea)$_2$] (1). Into suspension of PtI_2 (0.05 g, 0.10 mmol) in 10 ml of water 10.40 μl (0.20 mmol) of 2-hydroxyethylamine was added. The solution was stirred at 60–70 °C for several hours. p*H* was kept at 4.5–5.0 by adding of 0.10 M $HClO_4$. The color of the solution was changed from dark-violet to dark-yellow and was left at room temperature to evaporate (Scheme 1). The dark-yellow needles crystals were obtained (yield 36.6 mg, 64 %). Recrystallization was from methanol:water (60/40, *v/v*). Found: H 2.40, C 8.51, N 4.99 %. $C_4H_{14}I_2N_2O_2Pt$ requires H 2.47, C 8.41, N 4.91 %. IR (KBr) ν_{max} cm^{-1}: 3400 ν(O-H), 3100 ν(N-H), 2850–2900 ν(C-H) 1560–1620 δ(N-H). UV-Vis λ_{max} nm: 390.47. ^{1}H NMR (200 MHz, D_2O) δ_H ppm: 3.82 (2H, *t*, CH_2-OH, *J* = 5.27 Hz), 3.14 (2H, *t*, CH_2-NH_2, *J* = 5.27 Hz).

trans-[PtCl$_2$(dea)$_2$] (2). Into aqueous solution of $K_2[PtCl_4]$ (0.1 g, 0.24 mmol) 50 μl (0.48 mmol) of 2,2'-dihydroxydiethylamine was added. The solution was stirred at 60–70 °C for several hours. p*H* was kept at 4.5–5.0 by adding of 0.10 M $HClO_4$. The color of the solution was changed from dark-red to dark-orange and was left at room temperature to evaporate (Scheme 2). The dark-orange crystals were obtained (yield 60.6 mg, 53 %). The complex was recrystallized from 5 ml mixture of the methanol:water (50/50, *v/v*). Found: H 4.59, C 20.03, N 5.92 %. $C_8H_{22}Cl_2N_2Opt$ requiers H 4.66, C 20.18, N 5.88 %. IR (KBr) ν_{max} cm^{-1}: 3412 ν(O-H), 3200 ν(N-H), 2970-2940 ν(C-H), 1618-1650 δ(N-H). UV-Vis λ_{max} nm: 384.02. ^{1}H NMR (200 MHz, D_2O) δ_H ppm: 3.88 (2H, *t*, CH_2-OH, *J* = 5.4 Hz), 3.25 (2H, *t*, CH_2-NH_2, *J* = 5.4 Hz).

Structure Determination

Crystallographic data for complexes **1** and **2** are summarized in Table 1. X-Ray diffraction data were collected at 100 K on a Bruker-Nonius KappaCCD diffractometer using MoKα radiation (λ = 0.71073 Å, graphite monochromator). Absorption corrections were performed on a semi-empirical basis from multiple scans with SADABS.[6] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 in the anisotropic approximation for all atoms except hydrogen. Space groups were assigned according to the numbers in International Tables.[6] The complex molecule of ***trans*-[PtCl$_2$(dea)$_2$]** (**2**) was situated on a fourfold symmetric crystallographic site (Wyckoff position 4*a* with a 2/*m* site symmetry). The OH^- group was disordered with a refined occupancy of the two alternative sites of 46(2) and 54(2) %. Attempts to refine the data in space group $P4_2/mcm$ resulted in disorder of all atoms except Pt, significantly worse values and geometric parameters. All hydrogen atoms were placed in positions of optimized geometry. The isotropic displacement parameters of the H atoms were tied to those of their adjacent carrier atoms by a factor of either 1.2 or 1.5.

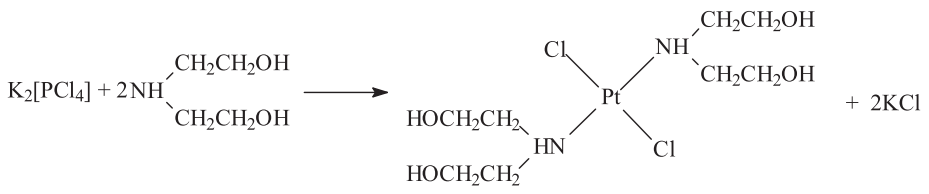
In the structure of *trans*-[$PtI_2(mea)_2$] complex the atoms around the platinum center are arranged in a square-planar manner (Figure 1). The Pt(1)-N(1), Pt(1)-N(2), Pt(1)-I(1) and Pt(1)-I(2) distances are in the normal range.[5] The angular sum of equatorial atoms are 360.01°. The N(1)-Pt(1)-N(2) and I(1)-Pt(1)-I(2) angles are 179.56(12) and 177.392(9), respectively. The small deformation of the I(1)-Pt(1)-I(2) angle from the ideal value of 180° is due the space requirements of the I^- ligands (Table 2).

The N-H group participates in a interaction leading to an intermolecular N(1)-H(1*A*)···O(1) hydrogen bond in complex (**1**) (Table 3).

In the structure of *trans*-[$PtCl_2(dea)_2$] complex the coordination sphere of the central Pt(II) ion is comprised by two nitrogen donor atoms (from two 2,2'-dihydroxydiethylamine ligands) *trans* to each other and two chlorido ligands also in *trans* position. The molecule itself is located on a crystallographic twofold axis parallel to the *z*-direction and exhibits therefore C_2 symmetry (Figure 2). The geometry of the complex is almost ideally square-planar.

The Pt-N (2.041(7) Å) and Pt-Cl (2.302(2) Å) distances are in the range of distances reported previously for the isomorphous Pd(II) analog (Table 4).[7]

Scheme 1. Synthesis of *trans*-diiodidobis(2-hydroxyethylamine)platinum(II).



Scheme 2. Synthesis of *trans*-dichloridobis(2,2'-dihydroxydiethylamine)platinum(II).

Table 1. Crystal data, data collection and refinement details for (**1**) and (**2**).

	trans-[$PtI_2(mea)_2$] (**1**) CCDC-2015320	*trans*-[$PtCl_2(dea)_2$] (**2**) CCDC-2015319
Molecular Formula	$C_4H_{14}I_2N_2O_2Pt$	$C_8H_2Cl_2N_2O_4Pt$
Mol. Weight	571.06	476.27
Color, shape	dark-yellow, needles	dark-orange, block
Crystal size (mm)	0.20×0.11×0.07	0.28×0.22×0.18
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P4_2/mbc$
a (Å)	9.757(1)	9.8624(6)
b (Å)	14.719(2)	9.8624(6)
c (Å)	8.246(1)	14.2998(9)
β (°)	98.07(1)	90
V / (Å^3)	1172.5(2)	1390.9(2)
Z	4	4
d_{calc} (mg/m^3)	3.235	2.274
μ (mm^{-1})	17.200	10.477
F(000)	1008	912
T_{min}; T_{max}	0.123; 0.300	0.062; 0.150
θ range for data collection (◦) Limiting indices	3.48–29.57 $-13 \le h \le 13$ $-20 \le k \le 20$ $-11 \le l \le 11$	4.08–28.70 $-13 \le h \le 13$ $-13 \le k \le 11$ $-19 \le l \le 19$
Reflection collected	19792	19860
Independent reflection	3232 (R_{int} = 0.0327)	939 (R_{int} = 0.0483)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Refined parameters	103	62
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Goodness-of-fit on F^2 (all data)	1.156	1.329
Final R indices [$I_o > 2\sigma(I)$]	R_1 = 0.0210, wR_2 = 0.0386	R_1 = 0.0266, wR_2 = 0.0638
R indices (all data)	R_1 = 0.0287, wR_2 = 0.0398	R_1 = 0.0366, wR_2 = 0.0671
Extinction coefficient	0.00062(5)	/
Largest diff. peak and hole (eÅ $^{-3}$)	0.941; –0.900	0.843; –1.249

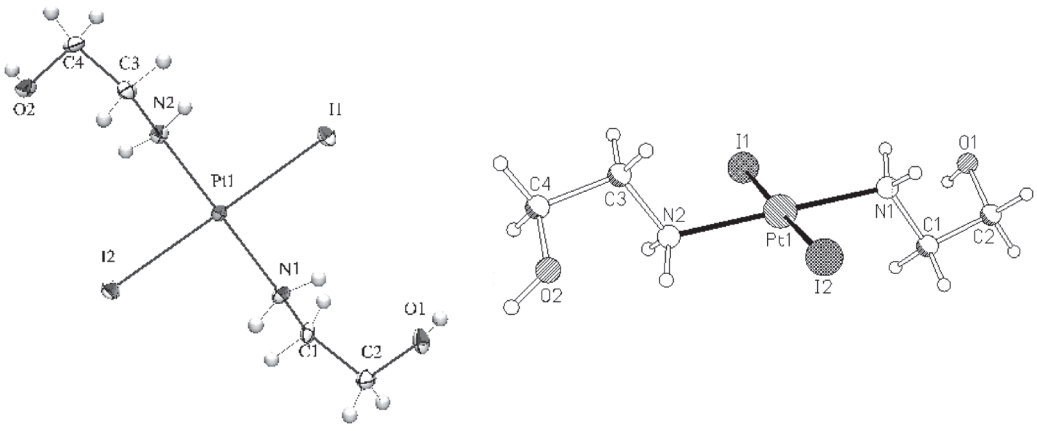


Figure 1. ORTEP drawing (left) and ball-and-stick representation (right) of complex (**1**) with the applied atomic numbering scheme and thermal ellipsoids at 50 % probability level and H atoms are shown as small spheres or arbitrary radii.

Table 2. Selected bond dinstances (Å) and angles (°) for *trans*-[$PtI_2(mea)_2$] complex.

Distances (Å)		Angles (°)	
Pt(1)-N(1)	2.048(3)	N(1)-Pt(1)-N(2)	179.56(12)
Pt(1)-N(2)	2.052(3)	N(1)-Pt(1)-I(1)	89.34(9)
Pt(1)-I(1)	2.6005(4)	N(2)-Pt(1)-I(1)	90.81(9)
Pt(1)-I(2)	2.6041(4)	N(1)-Pt(1)-I(2)	90.53(9)
O(1)-C(2)	1.426(5)	N(2)-Pt(1)-I(2)	89.34(9)
O(2)-C(4)	1.431(5)	I(1)-Pt(1)-I(2)	177.392(9)
N(1)-C(1)	1.492(4)	C(1)-N(1)-Pt(1)	117.0(2)
N(2)-C(3)	1.483(5)	C(3)-N(2)-Pt(1)	116.7(2)
C(1)-C(2)	1.515(5)	N(1)-C(1)-C(2)	109.7(3)
C(3)-C(4)	1.518(5)	O(1)-C(2)-C(1)	109.9(3)
		N(2)-C(3)-C(4)	110.5(3)
		O(2)-C(4)-C(3)	107.0(3)

The hydroxyl and N-H groups from the 2,2'-dihydroxydiethylamine are involving in very strong hydrogen bonding interaction between complex units (Table 5).

The crystal packing structure of *trans*-[$PtCl_2(dea)_2$] viewed down the crystallographic *b* axis is shown in Figure 3.

In both synthesized complexes the atoms around the platinum center are arranged in a square-plannar manner. The X-ray study confirmed almost ideal square--planar geometry for the *trans*-[$PtI_2(mea)_2$] complex. In the complex *trans*-[$PtI_2(mea)_2$] a small deformation of the I(1)-Pt(1)-I(2) angle is observed due the space requirements of the I^- ligands. Both structures are stabilized by intramolecular hydrogen bonds related to hydroxyl and chlorido groups which act as acceptors or donors for hydrogen bonds.

Table 3. Geometrical parameters for hydrogen bond for (**1**) complex.

Hydrogen bond	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(D-H···A) (°)
(**1**) N(1)-H(1A)···O(1)	0.91	2.40	2.8434(4)	110

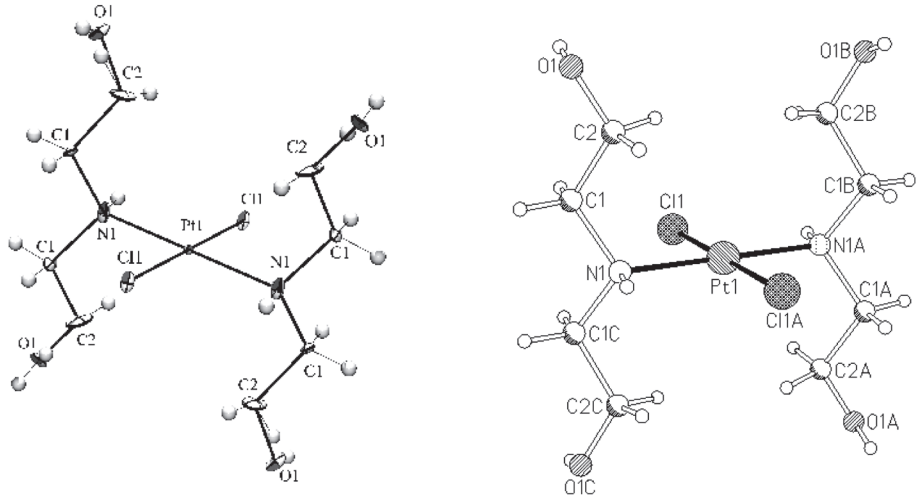


Figure 2. ORTEP drawing (left) and ball-and-stick representation (right) of complex (**2**) with the applied atomic numbering scheme and thermal ellipsoids at 50 % probability level and H atoms are shown as small spheres or arbitrary radii.

Table 4. Selected bond distances (Å) and angles (°) for *trans*-[$PtCl_2(dea)_2$] complex.

Distances (Å)		Angles (°)	
Pt(1)-N(1)#1	2.041(7)	N(1)#1-Pt(1)-N(1)	180.0
Pt(1)-N(1)	2.041(7)	N(1)#1-Pt(1)-Cl(1)	87.8(2)
Pt(1)-Cl(1)	2.302(2)	N(1)-Pt(1)-Cl(1)	92.2(2)
Pt(1)-Cl(1)#1	2.302(2)	N(1)#1-Pt(1)-Cl(1)#1	92.2(2)
O(1)-C(2)	1.312(15)	N(1)-Pt(1)-Cl(1)#1	87.8(2)
O(1')-C(2)	1.297(11)	Cl(1)-Pt(1)-Cl(1)#1	180.0
N(1)-C(1)	1.519(7)	C(1)-N(1)-C(1)#2	107.4(6)
N(1)-C(1)#2	1.519(7)	C(1)-N(1)-Pt(1)	114.8(4)
C(1)-C(2)	1.520(8)	C(1)#2-N(1)-Pt(1)	114.8(4)
		N(1)-C(1)-C(2)	110.2(5)
		O(1')-C(2)-O(1)	87.9(7)
		O(1')-C(2)-C(1)	113.7(7)
		O(1)-C(2)-C(1)	117.5(8)

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Dedication

This communication is dedicated to 75th birthday of extraordinary scientist and person Professor em. Dr. Dr. h. c. mult. Rudi van Eldik. The work is also dedicated to the memory of my great mentor, good person and excellent chemist Professor Dr. Živadin D. Bugarčić (1954–2017). T. V. Soldatović as a PhD student was witness of strong friendship between them. Thanks to Professor Dr. Živadin D. Bugarčić she was lucky to meet and to be part of Rudy's research group.

Table 5. Geometrical parameters for hydrogen bond for (**2**) complex.

Hydrogen bond	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(D-H···A) (°)
N(1)-H(1A)...Cl(1)#3	0.93	2.86	3.484(7)	124.0

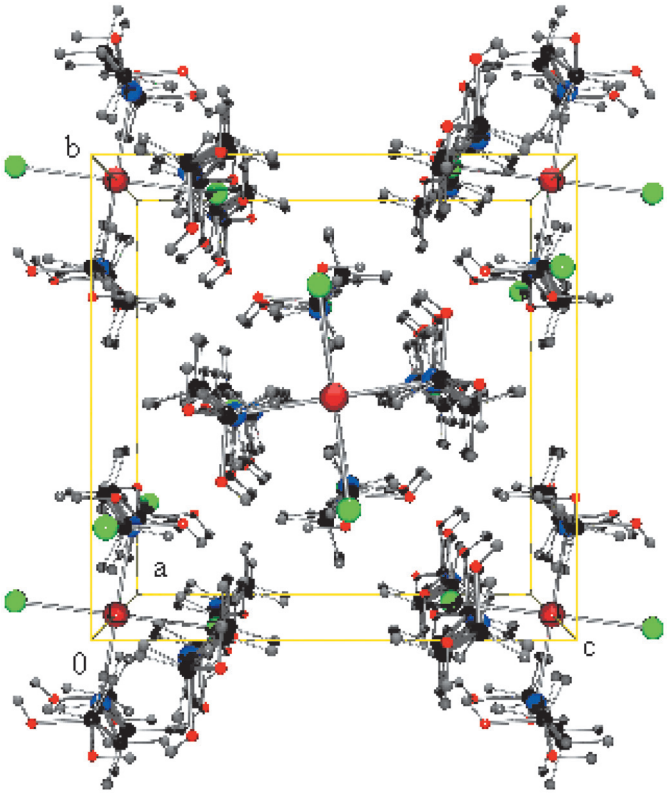

Figure 3. Packing diagram in the unit cell of complex (**2**).

Crystallographic information: CCDC-2015320 for **1** and CCDC-2015319 for **2** contain the supplementary crystallographic data for compounds **1**-**8**, respectively, in this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

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