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STRUCTURES OF Pd(II) COMPLEXES WITH 5,7-SUBSTITUTED HALOGENDERIVATIVES OF 8-HYDROXYQUINOLINE

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Introduction

Cancer, as one of the biggest health hazard for mankind, is still under a wide research all over the world. Despite the dramatic development of antitumor drugs, the cancer death rate has improved rarely. Cisplatin is considered as a parent compound in the group of metal-based anticancer agents. Clinical applications of cisplatin are, however, restricted due to the acquired cell resistance after continuous treatment and significant side effects. From currently important platinum-based anticancer agents, cisplatin, carboplatin, oxaliplatin, nedaplatin and lobaplatin are of reasonable interest [1].

Except the platinum coordination compounds, there is also much interest in the synthesis and designing of palladium drugs that can have increased pharmacological action with a decreased spectrum of side effects. As an example, investigation carried out on *trans*-palladium(II) complexes with chloroquine, which has been used as an antimalarial and anti-inflammatory drug, showed that coordination of the ligand to the palladium(II) atom increased the antitumor activity against four cancer cell lines [2]. Cytotoxicity of halogenated derivatives of quinolin-8-ol (XQs) has recently been investigated. The cytotoxicity of XQs was enhanced by the addition of copper or zinc and it is believed that these ligands serve as ionophores [3].

Keeping in mind all these promising results of palladium(II) complexes and XQ ligands, we decided to prepare square-planar complexes of Pd(II) with these ligands with the aim to enhance their anticancer activity comparing to ligands itself. In this paper we describe the structures of four neutral complexes of Pd(II) with XQ ligands: $[Pd(CQ)_2]$ (**1**) [4] (CQ = 5-chloro-7-iodo-quinolin-8-ol, clioquinol), $[Pd(dClQ)_2]$ (**2**) (dClQ = 5,7-dichloro-quinolin-8-ol), $[Pd(dBrQ)_2]$ (**3**) (dBrQ = 5,7-dibromo-quinolin-8-ol) and $[Pd(dIQ)_2]$ (**4**) (dIQ = 5,7-diiodo-quinolin-8-ol), as well as two ionic $NH_2(CH_3)_2[Pd(CQ)Cl_2]$ (**5**) and $HCQ[Pd(CQ)Cl_2]\bullet 2H_2O$ (**6**) [5] coordination compounds.

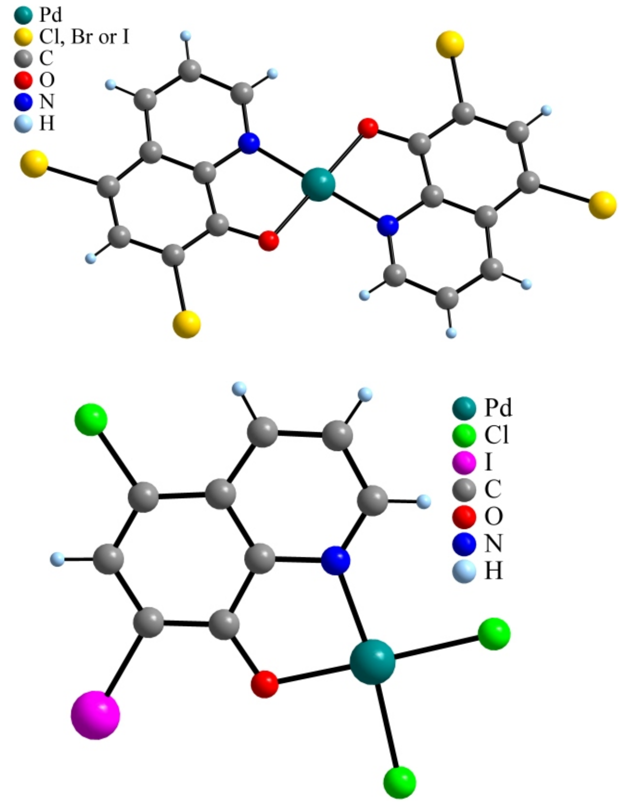

Figure 1. Structures of complexes **1** – **4** (top) and complex anion of **5** and **6** (bottom).

Results and discussion

The structures of complexes **1** – **4** (Fig. 1), are formed by neutral $[Pd(XQ)_2]$ molecules with two XQ molecules bidentately coordinated to Pd(II) atom by oxygen atom after deprotonation of XQ phenolic part and nitrogen atom of XQ pyridine part. There are two independent $[Pd(dClQ)_2]$ molecules in the structure of **2**. One of them is centrosymmetric with the Pd(II) atom occupying the center of symmetry, while the second one is pseudocentrosymmetric with the Pd(II) lying in a general position; the structures of **1**, **3** and **4** are all centrosymmetric. The values of Pd–O and Pd–N distances (1.995(3) Å and 1.990(3) Å for **1**; 2.002(6) Å and 1.992(5) Å in average, respectively for **2**; 2.001(2) Å and 1.993(3) Å, respectively for **3**; 1.985(9) Å and 2.010(10) Å, respectively for **4**) are slightly longer comparing to the previously studied square-planar complexes of CQ containing Ni(II) (1.851(2) Å and 1.883(2) Å, respectively) [6], and Cu(II) (1.919(6) Å and 1.974(15) Å, respectively) [7]. An increase of M–O and M–N distances (M = Ni, Cu and Pd) in the sequence Ni < Cu < Pd can be explained by an increasing covalent radius of these metals in the same sequence. Square-planar geometry around Pd(II) central atoms in the prepared complexes is more deformed than in the previously studied Ni and Cu complexes as the values of N–Pd–O angles (83.6(1)° in **1**; 83.6(2)° and 83.2(2)° in **2**; 83.31(9)° in **3** and 83.7(4)° in **4**) are lower than the corresponding N–M–O values (87.04(10)° for Ni, and 86.31° and 83.88° for Cu complexes) [6, 7].

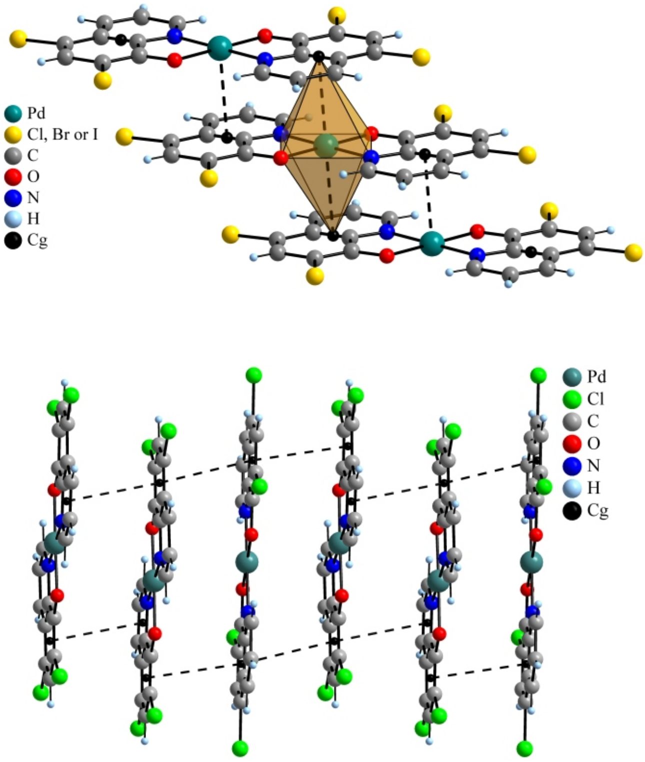

Figure 2. Long-range interactions (dashed lines) in **1**, **3** and **4** (top) and - interactions in **2** (bottom).

The molecular structures of the two ionic Pd(II) coordination compound (**5** and **6**) (Fig. 1) consist of discrete *cis*-$[PdCl_2(CQ)]^-$ anions in which the central Pd(II) atom has a distorted square-planar configuration with Pd–Cl distances of 2.2842(8) and 2.2997(7) Å in **5** and 2.271(1) and 2.311(1) Å in **6**, and with Pd–O and Pd–N distances of 2.013(2) and 2.014(2) Å, respectively in **5** and 2.035(3) and 2.009(4) Å, respectively in **6**. The negative charge of these anions is balanced by the presence of dimethylammonium cation or protonated molecule of CQ (HCQ^+) in **5** or **6**, respectively. The structure of **6** also involves two non-coordinated water molecules.

In addition, each structure is stabilized by long-range interactions. In **1**, **3** and **4** the interactions are on both sides of the molecular plane between the carbon atoms of the aromatic rings of contiguous molecules and Pd(II) atoms. The Pd(II) atoms and two adjacent centroids of aromatic rings lie in the perfect lines, thus the coordination number of Pd atoms in all three complexes can be considered as 4 + 2 with an elongated tetragonal bipyramidal coordination polyhedron (Fig. 2). Long-range interactions in **2** are different, as the structure of this complex consists of two independent $[Pd(dClQ)_2]$ molecules. These two molecules are interconnected by - interactions, which occur between the phenolic parts of adjacent dClQ ligands and pyridine and phenolic parts of another two dClQ molecules. An infinite neutral chain parallel with [010] is formed by stacking of $[Pd(dClQ)_2]$ molecules (Fig 2).

There are two kinds of - interactions in **5**, where a couple of anions is aligned analogically to an alignment in a graphite, *i.e.* centroid of one phenyl ring is exactly above the C5 atom of the adjacent phenyl ring. Upper anion of this pair is overlapped with another anion in such a way that centroid of the pyridine ring is exactly beneath the centroid of the C1–C2 bond and thus parallel displaced stacking of anions is formed (Fig. 3).

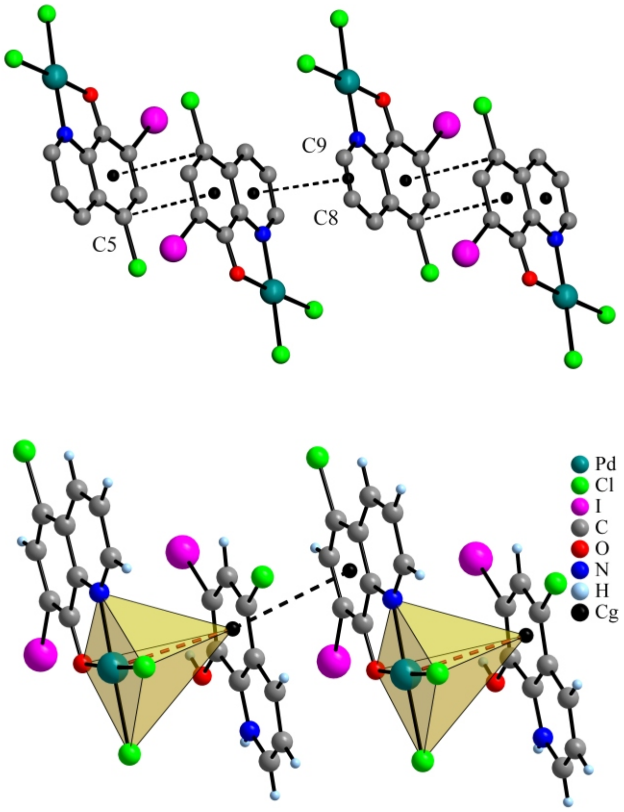

Figure 3. Long-range interactions (dashed lines) in **5** (top) and **6** (bottom).

- interactions in **6** occur between the phenolic parts of the complex anion and the cation. Moreover, the Pd(II) interacts with adjacent cation and possible ^{6} semi coordination of phenyl ring of the cation could be considered. Thus the coordination number of Pd(II) atom can be considered as 4+1 with a tetragonal pyramidal coordination polyhedron. Due to these intermolecular contacts the cations and anions are linked to form a chain parallel with [010] (Fig. 3).

Stability of the structure of **5** is also enhanced by a system of hydrogen bonds which involves both of the hydrogen atoms bonded to the nitrogen atom in dimethylammonium cation and a neutral infinite chain nearly parallel with [100] is formed (Fig. 4). Both uncoordinated water molecules in **6** interconnect the HCQ^+ cations *via* hydrogen bonds into a plane parallel with (100) (Fig. 4).

Acknowledgements

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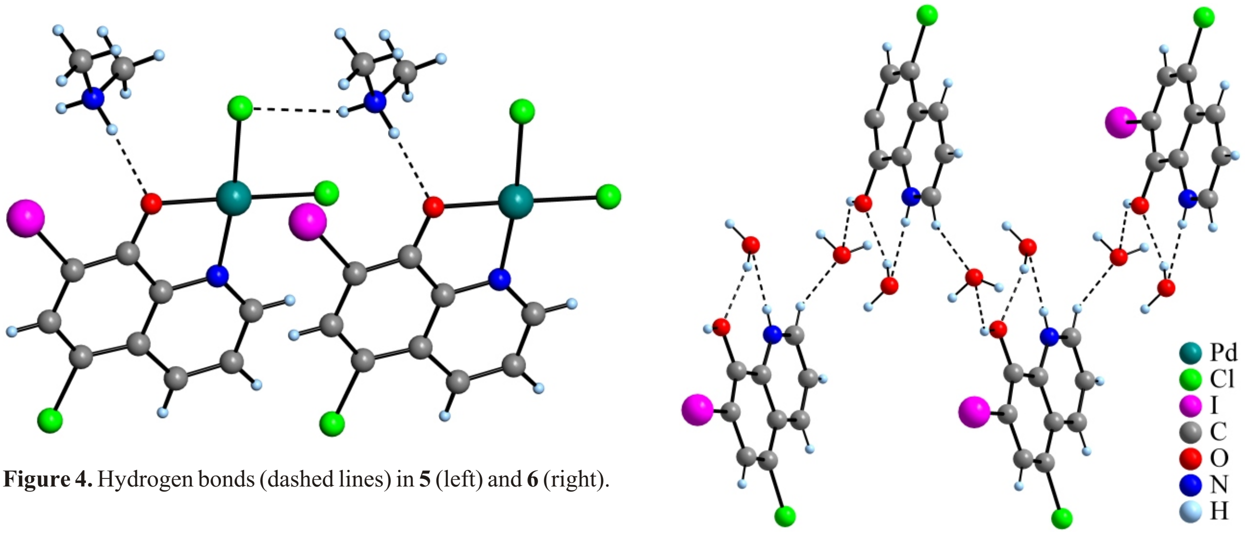

Figure 4. Hydrogen bonds (dashed lines) in **5** (left) and **6** (right).

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PENTACOORDINATED Cu(II) COMPLEXES WITH TRICYANOMETHANIDE, OR HOW DISAPPOINTED CAN BE THE RESULTS OF STRUCTURE ANALYSIS

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Introduction

The molecular structures of five-coordinated $[Cu(L)_2X]Y$ complexes (L = 1,10-phenantroline (phen) or 2,2'-bipyridine (bpy), X and Y = 1- anions) show an extensive variability ranging from trigonal bipyramid (TBP) to square pyramidal (TEP) stereochemistries, with majority complexes displaying a structure, which is in the range of these two extremes [1]. In our previous work we have prepared and studied complexes with $X = N(CN)_2^-$ and $ONC(CN)_2^-$ with the aim to characterize the shape of coordination polyhedra (SCP) around the Cu atoms [2, 3]. The obtained results showed that the preferred SCP for compounds with phen is close to TBP, whereas for SCP bpy compounds is close to TEP.

Tricyanomethanide (tcm) anion $C(CN)_3^-$ can coordinate similarly as $N(CN)_2^-$ and $ONC(CN)_2^-$ anions [4]. Therefore we decided to prepare complexes of general $[Cu(L)_2tcm]Y$ formula (L = phen or bpy and Y = ClO_4^-, NO_3^-, Br^- and Cl^-) and thus to continue in our previous work dealing with the SCP. In this paper we describe structures of ten ionic coordination compounds, which can be divided into three groups: a) $[Cu(L)_2tcm]tcm$: $[Cu(phen)_2tcm]tcm$ (**1**) and $[Cu(bpy)_2tcm]tcm$ (**2**); b) $[Cu(L)_2tcm]ClO_4$: $[Cu(bpy)_2tcm]ClO_4$ (**3**), $K[Cu(phen)_2tcm]_3tcm(ClO_4)_3$ (**4**) and $[Cu(phen)_2tcm][Cu(phen)_2H_2O]tcm(ClO_4)_2{\cdot}H_2O$ (**5**) and c) $[Cu(L)_2Y]tcm$: $[Cu(phen)_2NO_3]tcm$ (**6**), $[Cu(phen)_2Cl]tcm{\cdot}H_2O$ (**7**), $[Cu(bpy)_2Cl]tcm$ (**8**), $[Cu(phen)_2Br]tcm{\cdot}0{,}5H_2O{\cdot}0{,}5EtOH$ (**9**) and $[Cu(bpy)_2Cl]tcm{\cdot}H_2O$ (**10**).

Results and discussion

Complexes **1** and **2** (Fig. 1) belong to the first group. Their structures are formed by $[Cu(L)_2tcm]^+$ cations and non-coordinating tcm anions. The structure of the cations consists of two phen or bpy molecules and one tcm anion coordinated to a copper(II) atom.

The second group consists of complexes **3** - **5** (Fig. 2), which contain the same cations as the previous group, however to balance their positive charge, ClO_4 in **3** or ClO_4 and tcm anions in **4** and **5** are used. Moreover, structure of **4**