pozorovala existencia dvoch nevýrazných maxím pri hodnotách 135 a 163 , kým v prípade uhla N–H···F(BF_3^-) sa maximálna početnosť pozorovala v rozsahu uhlov 130-150°.

Následné experimentálne štúdium sústavy Cu(II) - *L–L* - BF_4^- viedlo k príprave a charakterizácii nových zlúčenín [Cu(*men*)$_2$(BF_4)$_2$] (**1**), [Cu(*bmen*)$_2$(BF_4)$_2$] (**2**) a [{Cu(OH)(H_2O)(*tmen*)}$_2$](BF_4)$_2$ (**3**).

Výsledky monokryštálovej štruktúrnej analýzy zlúčeniny **1** ukázali, že jej kryštálová štruktúra je tvorená molekulami [Cu(*men*)$_2$(BF_4)$_2$], v ktorých atóm Cu(II) je koordinovaný deformovane oktaedricky v tvare 4+2 dvoma molekulami chelátového liganda *men* v ekvatoriálnej rovine (priemerná hodnota Cu-N je 2,0243(12) Å), kým axiálne polohy obsadzujú monodentátne BF_4^- ligandy (Cu-F je 2,5091(11) Å) (Obr. 3). Kryštálová štruktúra **1** je stabilizovaná intra- a intermolekulovými vodíkovými väzbami typu N-H···F [9]. Výsledky sa diskutujú v prednáške.

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SL10

COMPLEXES OF NI(II) AND PD(II) WITH 8-HYDROXYQUINOLINE DERIVATIVES

P. Vranec, I. Potočňák

P. J. Šafárik University in Košice, Faculty of Science, Department of Inorganic Chemistry, Moyzesova 11, 041 54 Košice, SR, peter.vranec@student.upjs.sk, ivan.potocnak@upjs.sk

Introduction

Cancer is one of the major causes of death in many countries of the world. Cisplatin, as one of the leading metal-based drugs, is widely used in treatment of cancer, being especially effective against genitourinary tumours. Significant side effects and drug resistance, however, have limited its clinical applications. This perturbing news motivates us and many others to consider how to protect ourselves against cancer and as a consequence there is an increase in the design of new and more effective drugs to combat these diseases.

There are several ways how to increase the efficiency of metal organic drugs. One of them is to prepare a new drug in the form of a complex containing biologically active metal as a central atom and biologically active ligands which have adequate chelating properties and favourable toxicity profiles. This is generally true of the 8-hydroxyquinoline drug class.

One example is 5-chloro-7-iodo-quinolin-8-ol (clioquinol, CQ). CQ, a chelator of copper, zinc, and iron, has been used for many years as an antimicrobial agent. It was first prepared in Germany in the early part of the last century and was widely used as an antibiotic for the treatment of diarrhea and skin infection. Recently, clioquinol is producing very encouraging results in the treatment of Alzheimer's disease [1]. Its biological effects are most likely ascribed to complexation of specific metal ions, such as copper(II) and zinc(II), critically associated with protein aggregation and degeneration processes in the brain [2]. CQ also showed efficacy in an animal model of Parkinson's disease [3]. Moreover, it has been found that CQ is toxic against cancer cells and inhibits the growth of tumours [4]. Another example of anticancer active compounds of this type are bis-8-hydroxyquinoline substituted benzylamines, namely JLK 1472 and JLK 1486. Cytotoxic activity of these compounds was investigated on some human cancer cell lines and it has been found that many cancer cell lines are sensitive to both drugs. [5]

Interesting biological activity of 8-hydroxyquinoline derivatives (XQ) led us to an idea to prepare square-planar complexes of Ni(II), Pd(II) and Pt(II) with these ligands, which should mimic cisplatin. From the different types of syntheses we prepared 6 compounds in the form of monocrystals suitable for X-ray data collection so far. After confirming the presence of respective ligands by infrared spectroscopy and estimating composition of these complexes by elemental analysis, we studied the structures of these compounds. In this paper we describe the preparation and crystal structures of following complexes:

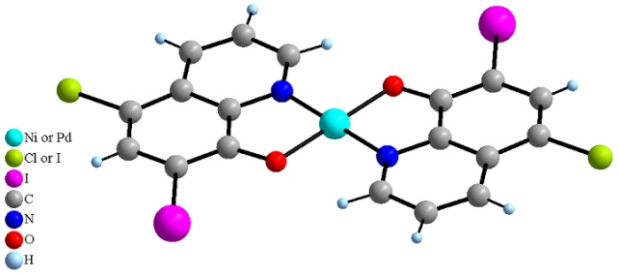

Figure 1. Structure of $[Ni(CQ)_2]$ (**1**), $[Pd(CQ)_2]$ (**3**) and $[Pd(dIQ)_2]$ (**6**) complexes.

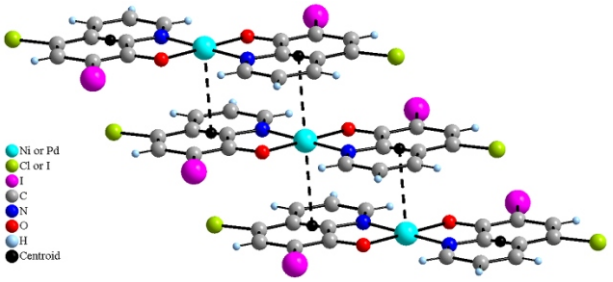

Figure 2. Stacking of the molecules in $[Ni(CQ)_2]$ (**1**), $[Pd(CQ)_2]$ (**3**) and [Pd(dIQ)2] (**6**) complexes.

$[Ni(CQ)_2]$ (**1**), $NH_2(CH_3)_2[Ni(CQ)_3]\cdot DMF\cdot H_2O$ (**2**) $[Pd(CQ)_2]$ (**3**), $NH_2(CH_3)_2[Pd(CQ)Cl_2]$ (**4**), $HCQ[Pd(CQ)Cl_2]\cdot H_2O$ (**5**) and $[Pd(dIQ)_2]$ (**6**), where dIQ = 5,7-diiodo-quinolin-8-ol, which we expect to have an increased biological activity.

Results and discussion

From the results of X-ray structural analysis of **1, 3** and **6** we can state that these three complexes are isostructural molecular compounds. Central atoms are coordinated by two *trans*-arranged molecules of XQ ligands in a square planar geometry (Fig. 1). The ligands are coordinated by nitrogen atoms of pyridine part and oxygen atoms of phenolic part after hydroxyl group deprotonation of respective ligands with M–O distances (Ni–O = 1.851(2) Å and Pd–O = 1.988(4) Å in average) slightly shorter than M–N ones (Ni–N = 1.882(2) and Pd–N = 2.004(8) Å in average) and with the distances around the Ni atom shorter than around the Pd atom.

Similar differences between M–O and M–N distances have been observed in $[Cu(CQ)_2]$ and $[Zn(CQ)_2(H_2O)]\cdot THF\cdot 0.5H_2O$ [2] as well as in Ni complexes with different quinolines [6, 7]. In addition, each nickel and palladium atoms in **1**, **3** and **6** form long-range interactions on both sides of the molecular plane with the carbon atoms of the aromatic rings of contiguous molecules. The distances between parallel mean planes of $[M(XQ)_2]$ molecules range between 3.336 and 3.401 Å, and the distances between centroids of the aromatic rings and Ni and Pd atoms span between 3.401 and 3.477 Å (corresponding values for the $[Cu(CQ)_2]$ complex [2] are 3.316 and 3.407 Å, respectively). Such interactions give rise to stacks of molecules. Moreover the M atoms (Ni or Pd) and two adjacent centroids lie in perfect lines which make angles with the $[M(XQ)_2]$ planes of 78.8, 77.6 and 76.1° for **1**, **3** and **6**, respectively (Fig. 2) (76.2° in the $[Cu(CQ)_2]$ complex [2]).

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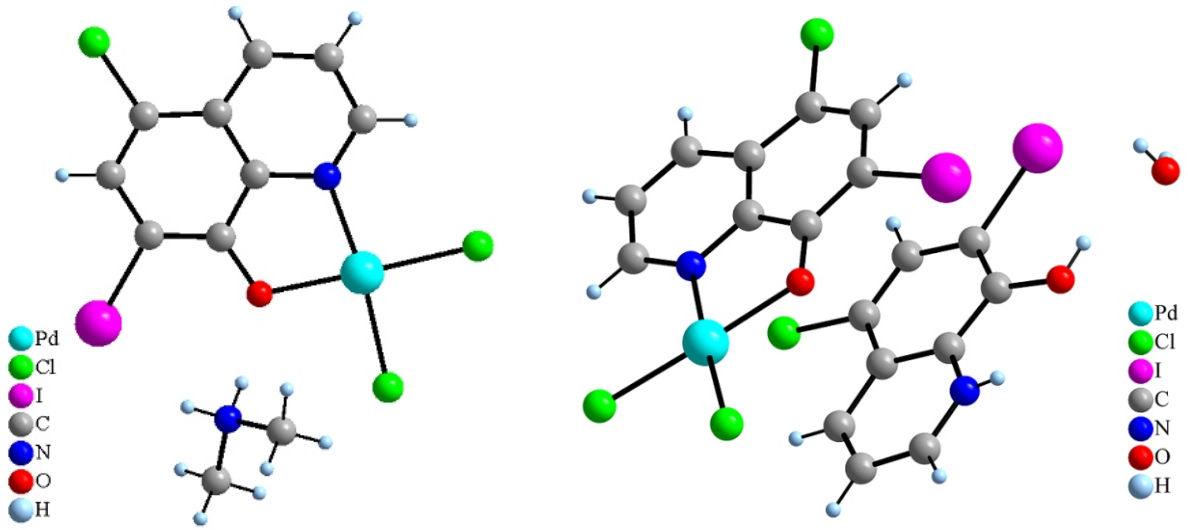

Figure 3. Structures of $NH_2(CH_3)_2[PdCl_2(CQ)]$ (**4**) (left) and $HCQ[Pd(CQ)Cl_2]\cdot H_2O$ (**5**) (right).

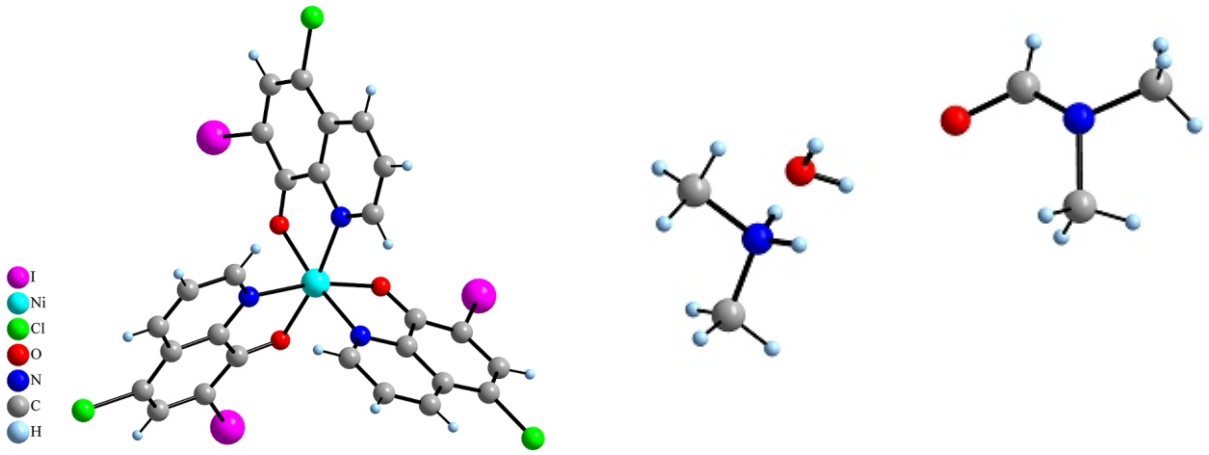

Figure 4. Structure of $[Ni(CQ)_3]^-$ complex anion (left) and $NH_2(CH_3)_2^+$ cation along with solvated molecules of DMF and H_2O (right).

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SL11

Contribution to study of crystal structure of Cu-Ni heterobimetalic coordination compounds

PRÍSPEVOK K ŠTÚDIU KRYŠTÁLOVÝCH ŠTRUKTÚR CU-NI HETEROBIMETALICKÝCH KOORDINAČNÝCH ZLÚČENÍN

I. Kočanová, J. Kuchár, M. Orendáč, V. Dankovičová, J. Černák

Katedra anorganickej chémie, Ústav chemických vied, Univerzita P.J. Šafárika,, Moyzesova 11, 041 54 Košice, SR, ivana.kocanova@gmail.com

Štúdium magnetických vlastností koordinačných zlúčenín predstavuje v súčasnosti jeden z hlavných smerov výskumu v koordinačnej chémii. Záujem o štúdium magnetických vlastností koordinačných zlúčenín je motivovaný jednak snahou pochopiť súvis medzi štruktúrou, zložením a magnetickými vlastnosťami látok, jednak potenciálnymi aplikačnými možnosťami. Jednu skupinu látok zaujímavých z magnetického hľadiska predstavujú také koordinačné zlúčeniny, v ktorých sa striedajú centrálne atómy s rôznym spinom, ktoré v prípade jednorozmerných (1D) látok sa nazývajú alternujúce reťazce. Alternujúce reťazce je možné chemicky realizovať dvoma spôsobmi: (1) paramagnetické centrálne atómy v reťazci sú rovnaké, ale sú pospájané striedavo dvoma rozdielnymi mostíkovými molekulami alebo iónmi (alternujú sa mostíky), alebo (2) v reťazci sa striedajú rôzne centrálne atómy (alternujú spiny magnetických iónov), ktoré sú pospájané rovnakými mostíkovými molekulami alebo iónmi. Pre druhú možnosť v prípade striedania centrálnych atómov so spinom $S_1 = 1/2$ a s väčšou hodnotou spinu, napr. $S_2 = 1$ existuje predpoveď, že pri dostatočne nízkej teplote T, to je pri teplote nižšej ako je hodnota konštanty výmennej interakcie J ($T < J$), sa takáto látka bude chovať ako látka s feromagnetickou interakciou napriek tomu, že interakcia bude antiferomagnetická. Teoreticky sa študovali takéto systémy s centrálnymi atómami Cu(II) a Ni(II) a existuje teda predpoveď tvaru teplotnej závislosti magnetickej susceptibility na teplote [1]. Z uvedeného sa javí zaujímavé pripraviť Cu-Ni heterobimetalické látky s uvedenou kombináciou spinov a charakterizovať ich spektrálnymi metódami, určiť ich kryštálové štruktúry a následne študovať ich magnetické vlastnosti a tie porovnať s teoretickou predpoveďou.

Analýzou údajov z Cambridgeskej kryštalografickej databázy (CSD) [2] a Databázy anorganických kryštálových štruktúr (ICSD) [3] sa zistilo, že v súčasnosti je popísaných celkove 253 heterobimetalických zlúčenín na báze medi a niklu s vyriešenou kryštálovou štruktúrou.