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Cyclometalated alkynylgold(III) complexes of 2-phenylpyridine and 2-(*p*-tolyl)-pyridine – Synthesis, photophysical and electroluminescence properties

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ABSTRACT

Two cyclometalated alkynylgold(III) complexes [AuCl(tpy)(C≡C–$C_6H_4CH_3$)] (**1**) and [AuCl(ppy)(C≡C–$C_6H_4CH_3$)] (**2**), where ppy = 2-phenylpyridine and tpy = 2-(*p*-tolyl)-pyridine, were successfully synthetized. Their photophysical properties were investigated by absorption and photoluminescence spectroscopy in solution, solid state, and glass matrix (77 K). Differences in solid state luminescent behaviour of the reported Au(III) complexes were correlated with packing of [AuCl(tpy)(C≡C–$C_6H_4CH_3$)] and [AuCl(ppy)(C≡C–$C_6H_4CH_3$)] molecules and weak interactions in the network lattices of **1** and **2**. Additionally, photoluminescence spectra of [AuCl(tpy)(C≡C–$C_6H_4CH_3$)] in film and dispersed in solid matrix consisting of poly(9-vinylcarbazole) and (2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazole) were registered. The preliminary tests of electroluminescence ability of complex **1** were carried out.

1. Introduction

In recent years, the interest in the coordination chemistry of gold (III), especially employing cyclometalated alkynyl complexes, has seen a significant increase. Gold(III) compounds have been studied for their cytotoxicity, catalytic activity, luminescence behaviour in the context of diverse promising applications as functional materials in optoelectronics and bioimaging.

Au(III) ion is isoelectronic with Pt(II), and both metal complexes feature a square planar configuration. These similarities have led to the assumption that gold(III) complexes might have analogous biological activity to cisplatin, and they have been proposed as candidates for development of a highly promising class of potential anticancer agents. Compared with platinum(II), however, gold(III) complexes have some disadvantages, including light-sensitivity in solution and instability under physiological conditions, predominantly because of their high reduction potential and fast rate of hydrolysis. Nevertheless, the significant antiproliferative effects of several Au(III) complexes against a number of cancer cells have been evidenced in several *in vitro* studies [1]. Especially promising results were achieved for complexes containing multidentate N- and N,C-donor ligands with σ-bonded aromatic ring, which turned out to be stable in reducing biological media. These complexes exhibit cytotoxicity *in vitro* against MOLT-4 (human leukemia) and C2C12 (mouse tumor) cells [2], inhibit hepatocellular carcinoma *in vivo* [3] and inhibit growth of cisplatin-resistant ovarian cancer [4]. In addition, the capability of gold(III) complexes to interact with DNA, similar to platinum(II) analogues but with different mechanism of action, has been reported [5].

Since 1991, when Fukuda and Utimoto reported the catalytic hydration of alkynes by $Na[AuCl_4]$ [6], gold(III) complexes have been also widely explored towards hydration of alkynes [7], cycloisomerization [8], cyclization [9], nucleophilic substitution of alcohols [10], and electrophilic π-activation of unsaturated carbon-carbon bonds (alkynes, enynes, alkenes, allenes, etc.) toward nucleophiles [11].

The recent intensification of research toward development of new gold(III) luminophores for applications in efficient organic light-emitting devices (OLEDs) is predominately attributed to the utilization of different cyclometalating ligands in combination with the σ-donating alkynyl ligands. This concept has allowed to enhance the luminescence of the gold(III) based systems by decreasing the probability for the

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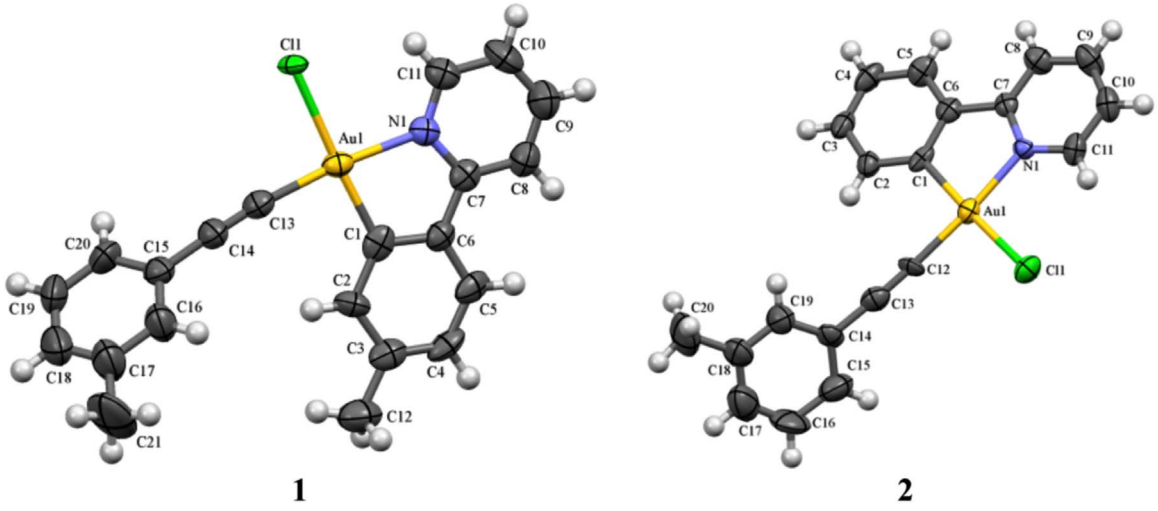

Fig. 1. Perspective views showing the molecular structures of **1** and **2** with the atom numbering. Displacement ellipsoids are drawn at 50% probability.

thermal population of the non-emissive d-d states [12].

Herein, we report the synthesis of two cyclometalated alkynylgold (III) complexes [AuCl(tpy)(C≡C–$C_6H_4CH_3$)] (**1**) and [AuCl(ppy)(C≡C–$C_6H_4CH_3$)] (**2**), where ppy = 2-phenylpyridine and tpy = 2-(*p*-tolyl)-pyridine. The obtained materials were thoroughly characterized using optical techniques, while strong electroluminescence signal measured in OLED geometry suggests potential for applying these structures as building blocks in optoelectronic devices.

2. Results and discussion

2.1. Synthesis and characterization

The alkynylgold(III) complexes [AuCl(tpy)(C≡C–$C_6H_4CH_3$)] (**1**) and [AuCl(ppy)(C≡C–$C_6H_4CH_3$)] (**2**) were prepared by reacting the respective [$AuCl_2$(tpy)] or [$AuCl_2$(ppy)] [13] with 3-ethynyltoluene in dichloromethane/acetonitrile mixture in the presence of a catalytic amount of copper(I) iodide in triethylamine. The identities of **1** and **2** were confirmed by ^{1}H NMR spectroscopy, elemental analysis, and X-ray crystallography (see Figs. S1-S2 in Supplementary material). The IR spectra of the complexes exhibited an absorption at 2154 cm^{-1} for both **1** and **2**, which is consistent with the presence of the alkynyl ligand in the terminal σ-coordination mode [12a,14] (see Figs. S3 and S4 in Supplementary material).

2.2. X-Ray crystal structures

Perspective views showing the molecular structures of **1** and **2** with the atom numbering are presented in Fig. 1. The selected bond lengths and angles for all structures are provided in Table 1, while the crystallographic data of **1** and **2** are summarized in Table S1 in Supplementary material.

In both compounds, the gold atom displays a distorted square planar coordination, typical of d^8 metal complexes. The maximum distance from the least squares plane defined by Au(1), N(1), C(1), C(13)/or C(12) and Cl(1) is +0.044(7) Å for C(1) in **1** and −0.0014(35) Å for N(1) and C(12) in **2**. The deviation from the ideal 90° is attributed to geometrical constraints issued by the occurrence of the five-member chelate ring of the bidentate 2-(*p*-tolyl)-pyridine (tpy) or 2-phenylpyridine (ppy) ligand. The C(1)−Au(1)−N(1) angle is 80.8(4) in **1** and 81.6(4)° in **2**. This is accompanied by the noticeable enlargement of the Cl(1)–Au(1)–N(1) angle, 96.3(2)° in **1** and 95.5(2)° in **2**. The Au–C≡C angles are 173.0(10)° in **1** and 175.9(10)° in **2**, forming a slightly distorted linear arrangement. The R-substituent ring of the alkynyl ligand is inclined to this plane at 54.31 in 1 and 55.86° in **2**. The chloride is *trans*-located to the carbon atom of the chelating cyclometalated ligand (N^C), and as it can be expected, no real deviation in the Au–Cl bond length with the change of the cyclometalating core was observed. The Au–Cl (2.455(2) Å in **1** and 2.356(3) Å in **2**), Au–N (2.070(8) Å in **1** and 2.053(8) Å in **2**), Au–$C_{ppy/ppy}$ (2.007(12) Å in **1** and 2.014(9) Å in **2**) and Au–$C_{alkynyl}$ (1.962(12) Å in **1** and 1.974(11) Å in **2**) bond lengths are rather expected and they correlate well with the values reported for the related cyclometalated alkynylgold(III) complexes (see Table S2 in Supplementary material). The intermolecular Au···Au distances of 5.1538(6) Å for **1** and 5.0530(6) Å for **2** were found to be longer than the sum of van der Waals radii for two gold(III) centers [15], revealing that no significant Au···Au interactions occurred in the crystal lattices of the complexes.

As shown in Fig. 2, the molecules [AuCl(tpy)(C≡C–$C_6H_4CH_3$)] and [AuCl(ppy)(C≡C–$C_6H_4CH_3$)] are arranged into an extended columnar array by Au•••π interactions in **1** and Au•••π and π•••π interactions in **2**. In both crystal lattices, [AuCl(N∧C)](C≡CR)] moieties are stacked in head-to-tail arrangement, preventing from short Au^{III}•••Au^{III} contacts. The intra- and intermolecular contacts detected in the structures **1** and **2** were collected in Tables S3-S5 in Supplementary material.

To analyse the molecular interactions in the crystal structures of **1** and **2**, Hirshfeld surface was also used [16]. A summary of the intermolecular contacts in the *tppz* crystal structures is provided in spots of Hirshfeld surfaces mapped with d_{norm} and in two-dimensional (2D) fingerprint plots (Fig. 3). The relative contributions of various intermolecular interactions to the Hirshfeld surfaces are illustrated in Fig. 4. The analysis revealed higher contribution of Cl•••H and Au•••π, but lower participation of Au••• π in the crystal structure **1** compared to **2**.

Table 1
Bond lengths [Å] and angles [°] for **1** and **2**.

	1 (X = 13)	**3** (X = 12)
Bond lengths		
Au(1)–Cl(1)	2.455(2)	2.356(3)
Au(1)–N(1)	2.070(8)	2.053(8)
Au(1)–C(1)	2.007(12)	2.014(9)
Au(1)–C(X)	1.962(12)	1.974(11)
Bond angles		
Cl(1)–Au(1)–N(1)	96.3(2)	95.5(2)
Cl(1)–Au(1)–C(1)	177.0(3)	177.2(3)
N(1)–Au(1)–C(1)	80.8(4)	81.6(4)
Cl(1)–Au(1)–C(X)	90.2(3)	89.6(3)
N(1)–Au(1)–C(X)	173.3(4)	174.9(3)
C(1)–Au(1)–C(X)	92.7(5)	93.2(5)