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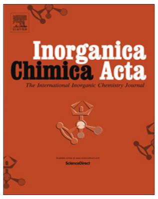

Research paper

Homoleptic mono- and dinuclear complexes of platinum(II) with 1,8-naphthyridine

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ABSTRACT

Two unprecedented, homoleptic Pt-1,8-naphthyridine complexes have been prepared and characterized. Reaction between 1,8-naphthyridine (napy) and a platinum(II) precursor leads to a mononuclear homoleptic platinum(II) complex with stoichiometry $[Pt(napy)_4](OTf)_2$. On the contrary, reaction between napy and a dinuclear platinum(III) precursor produces instead a rare example of a dinuclear, homoleptic, tetracationic platinum(II) complex with stoichiometry $[Pt_2(napy)_4](OTf)_4$. Crystal structures of both complexes have been obtained. The redox behavior of the dinuclear complex has been studied by cyclic voltammetry, in order to establish its suitability as model precatalyst for organometallic reactions exploiting the Pt(II)/Pt(IV) or Pt(II)/Pt(III) manifold.

1. Introduction

1,8-Naphthyridine and its derivatives represent a class of heterocycles which, beside their long recognized applicability as active ingredients in the medicinal and pharmacological field [1], also enjoy considerable popularity as ligands for metal centers, especially transition metals and rare earths [2,3]. The syn arrangement of the two nitrogen atoms at short distance (2.2 Å) renders 1,8-naphthyridine potentially suitable to coordinate in different fashions, namely monodentate [4], bidentate chelating [5], or bidentate bridging [2]; different coordination modes can even coexist in metal complexes featuring more than one ligand of this kind [6]. Furthermore, 1,8-naphthyridine has been functionalized with various additional neutral or even anionic coordinating groups, which may or may not be conjugated to the heterocyclic π system; the resulting polydentate ligands have been extensively utilized in the preparation of novel mono- and polynuclear complexes [2,7]. On the other hand, the number of homoleptic complexes of simple 1,8-naphthyridine with transition metal centers is quite limited [3] and several complexes reported in the first pioneering studies dating back to the early 1970s have not been structurally characterized, hence the actual coordination mode of 1,8-naphthyridine in those complexes is often not well established.

We have a longstanding interest in the preparation and use as catalysts of homoleptic, lantern-shaped, cationic dirhodium(II) complexes with 1,8-naphthyridine [8]. With this work, we extend our investigations to platinum(II), for which to the best of our knowledge no prior examples of homoleptic complexes with 1,8-naphthyridine are known. Our aim was in particular the preparation of dinuclear platinum(II) complexes with 1,8-naphthyridine as supporting bridging ligand, since dinuclear complexes exhibiting two stacked square planar platinum(II) centers at close distance are interesting potential precatalysts for reactions exploiting the Pt(II)/Pt(IV) or Pt(II)/Pt(III) manifold [9a], as well as models for oganometallic reactions involving related high oxidation state Pd catalysts [9b].

2. Results and discussion

Direct reaction of a convenient mononuclear platinum(II) precursor such as K_2PtCl_4 with 4 equivalents of 1,8-naphthyridine (hereafter simply termed napy) and subsequent removal of chloride anions with AgOTf yielded the homoleptic mononuclear dicationic complex $[Pt(napy)_4](OTf)_2$ **1** as a stable single reaction product (Scheme 1).

The complex was spectroscopically characterized and exhibited in its ^1H NMR spectrum the expected set of six different multiplets, only one of which, corresponding to the proton adjacent to Pt, showed coupling with ^{195}Pt. This is consistent with napy coordinating in a monodentate fashion to Pt and with the complex being nonfluxional, i.e. the Pt center does not switch between the two coordinating nitrogens of the same napy ligand, as occasionally observed with other Pt-napy complexes with monocoordinated napy [10].

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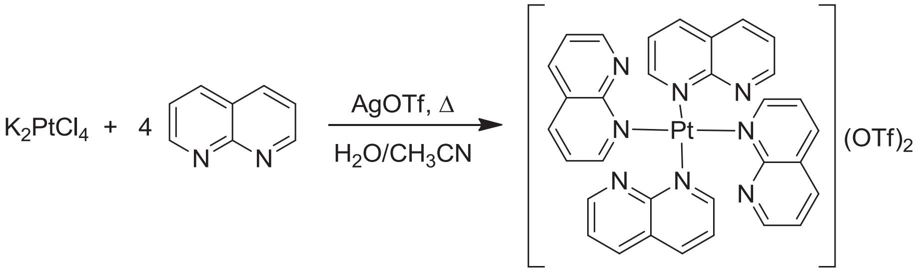

1

Scheme 1. Synthesis of the homoleptic, mononuclear Pt-napy complex **1**.

Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution. The unit cell of compound **1** comprises a $[Pt(napy)_4]^{2+}$ cation and two trifluoromethanesulfonate anions. The ORTEP view of the cation moiety is shown in Fig. 1 together with the atomic numbering scheme. Selected bond distances and angles are reported in the caption. The platinum(II) atom lies as expected in a square-planar geometry, defined by four N atoms of the napy ligands which form Pt-N bond distances spanning from 2.026(5) to 2.035(5) Å. For steric reasons each of the napy molecules is twisted out of the PtN_4 plane, forming dihedral angles of 82.79(2), 75.95(2), 88.20(2) and 87.05 (2)° for the N1-, N3-, N5- and N7-naphthyridine rings, respectively. The dihedral angle between the mean planes defined by N1- and N5-napy molecules measures 11.87(2)°, while 15.61(2)° is the dihedral mean angle between the N3- and N7-naphthyridine rings.

Each cationic complex is involved in weak CH…π interactions with adjacent molecules (Fig. 2), with C…C distances spanning from 3.696(3) to 3.750(3) Å. Moreover, the N1- and N5-naphthyridine rings exhibit weak π … π interactions between adjacent cationic complexes with a centroid to centroid distance of 4.070(3) Å as shown in the same figure. The oxygen atoms of the trifluoromethanesulfonate anions form interactions with CH groups of the napy molecules [C…O distances of 3.377(3) and 3.501(3) Å]. Considering the overall crystal packing, the cations tend to assemble into layers parallel to ab plane and the trifluoromethanesulfonate anions crystallize between the layers as shown in Fig. 3.

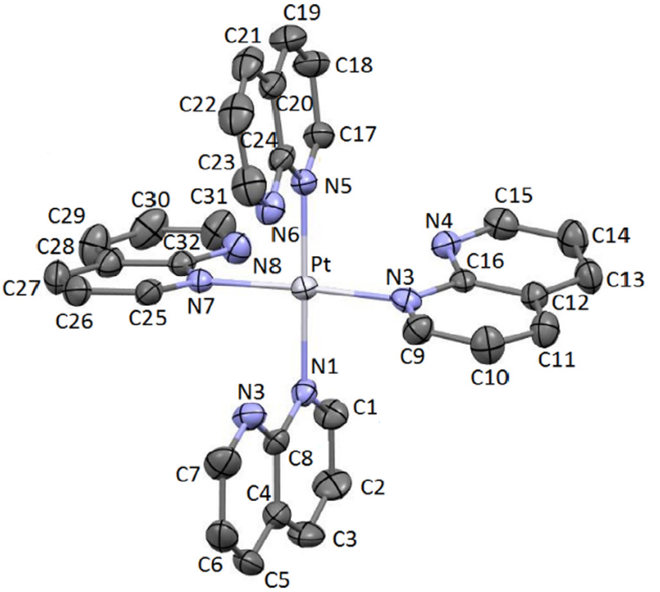

Fig. 1. ORTEP view of cationic compound in **1**. Ellipsoids are drawn at their 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): C1-N1 1.313(8), C8-N1 1.371(8), C7-N2 1.338(9), C8-N2 1.334(8), C9-N3 1.323(8), C16-N3 1.377(8), C15-N4 1.330(9), C16-N4 1.360(8), C17-N5 1.332 (8), C24-N5 1.385(8), C23-N6 1.317(9), C24-N6 1.341(9), C25-N7 1.325(8), C32-N7 1.374(8), C31-N8 1.323(9), C32-N8 1.361(8), N1-Pt 2.028(5), N3-Pt 2.028(6), N5-Pt 2.026(5), N7-Pt 2.035(5); N2-C8-N1 115.9(6), N4-C16-N3 115.5(6), N6-C24-N5 115.9(6), N8-C32-N7 116.7(6), N5-Pt-N3 93.0(2), N5-Pt-N1 177.1(2), N3-Pt-N1 88.4 (2), N5-Pt-N7 88.9(2), N3-Pt-N7 175.7(2), N1-Pt-N7 89.8(2).

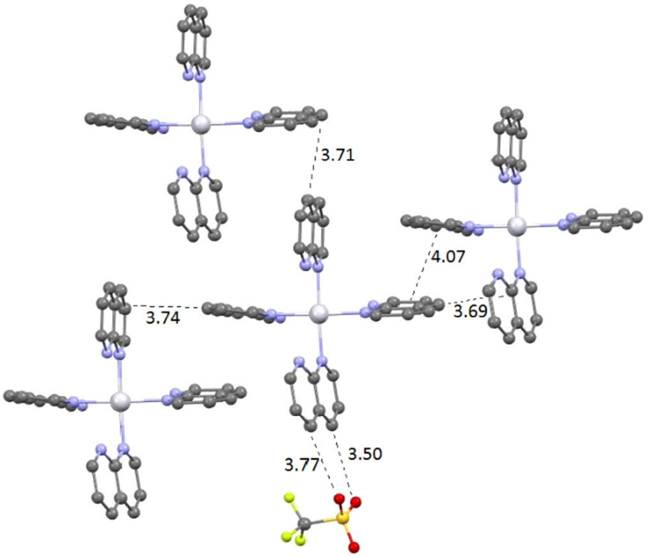

Fig. 2. Partial view of the crystal packing of compound **1** evidencing the interactions between adjacent molecules.

Attempts to prepare dinuclear platinum(II) complexes with bridging napy ligands starting from simple platinum(II) compounds or from complex **1** were unsuccessful. Consequently, we reverted to our previous experience with the preparation of homoleptic dinuclear rhodium(II)-napy complexes from dirhodium(II) acetate and envisaged to use as precursor the previously reported, isoelectronic diplatinum(III) complex $[Pt_2(\mu\text{-}OAc)_4(OH_2)_2](OTf)_2$ [11]. We first attempted the reaction of this complex with just 2 equivalents of napy, with the aim of accessing partially substituted dinuclear complexes, ideally bearing two acetates and two napy units as bridging ligands. The reaction proved ineffective in acetonitrile, and only the starting materials were recovered. However, on performing the reaction in acetic acid a complex product mixture was obtained, from which upon recrystallization the tetrasubstituted, tetracationic dinuclear complex **2** $[Pt_2(napy)_4](OTf)_4$ was isolated as a red crystalline solid in low yield (Scheme 2).

The ^1H NMR spectrum of **2** is as expected simpler than that of compound **1** and consists of only three different multiplets, as a