Journal of Molecular Structure 1085 (2015) 155–161

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis, crystal structure, theoretical calculations and antimicrobial properties of $[Pt(tetramethylthiourea)_4]\ [Pt(CN)_4]\cdot 4H_2O$

Haseeba Sadaf[a], Anvarhusein A. Isab[b], Saeed Ahmad[a,*], Arturo Espinosa[c,*], Míriam Mas-Montoya[c], Islam Ullah Khan[d], Ejaz[d], Seerat-ur Rehman[a], Muhammad Akhtar Javed Ali[a], Muhammad Saleem[e], José Ruiz[f,*], Christoph Janiak[g]

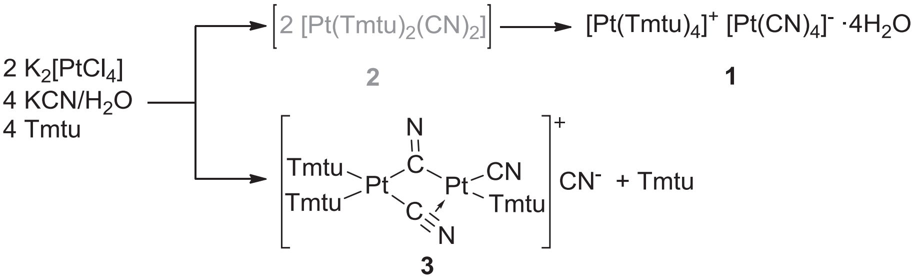
[a] *Department of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan*
[b] *Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*
[c] *Department of Organic Chemistry, Faculty of Chemistry, Campus de Espinardo, University of Murcia, 30071 Murcia, Spain*
[d] *Department of Chemistry, Government College University, Lahore 54000, Pakistan*
[e] *Department of Civil Engineering, Jubail University College, P. O. Box 10074, Jubail Industrial City 31961, Saudi Arabia*
[f] *Department of Inorganic Chemistry, Faculty of Chemistry, Campus de Espinardo, University of Murcia and Instituto Murciano de Investigación Biosanitaria, 30071 Murcia, Spain*
[g] *Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universität-Str. 1, 40204 Düsseldorf, Germany*

HIGHLIGHTS

- The synthesis and crystal structure of $[Pt(Tmtu)_4][Pt(CN)_4]$ is presented.
- Homodromic H-bonds of four H_2O molecules per unit cell determine a 2D-network.
- Complex $[Pt(Tmtu)_4][Pt(CN)_4]$ is moderately active against some microorganisms.
- Possible intermediacy of $[Pt(Tmtu)_2(CN)_2)]$ is evaluated by DFT calculations.
- Complex $[(Tmtu)_2Pt(\mu^2\text{-}CN)(\mu^2\text{-}\eta^2\text{-}CN)Pt(Tmtu)(CN)]CN$ was identified and characterized.

GRAPHICAL ABSTRACT

A new dinuclear platinum(II) complex formed by a $[Pt(Tmtu)_4]^{2+}$ cation (Tmtu = tetramethylthiourea) and a $[Pt(CN)_4]^{2-}$ anion is described and its higher stability with respect to a dimeric heterocoordinated $[Pt(Tmtu)_2(CN)_2)]$ species computationally evaluated.



ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 25 December 2014
Accepted 26 December 2014
Available online 5 January 2015

Keywords:
Platinum(II) complexes
Tetramethylthiourea
Cyanide
DFT calculations
X-ray structure

ABSTRACT

A new platinum(II) complex, $[Pt(Tmtu)_4][Pt(CN)_4]\cdot 4H_2O$ (**1**) was synthesized by reaction of $K_2[PtCl_4]$, KCN and tetramethylthiourea (Tmtu). Its structure was determined by X-ray crystallography. The $[Pt(CN)_4]^{2-}$ anion shows regular square planar geometry at platinum, while in the $[Pt(Tmtu)_4]^{2+}$ cation the geometry at platinum is somewhat distorted. Hydrogen bonding between water molecules and the cyanide nitrogen of $[Pt(CN)_4]^{2-}$ ions stabilizes the structure and leads to a supramolecular 2D network. DFT calculations support the experimentally found dinuclear (homocoordinated) ion-pair structure **1** as the most stable in comparison to noncovalent dimer $[Pt(CN)_2(Tmtu)_2]_2$ **2₂** that could, in turn, be involved in the formation sequence of **1**. Antimicrobial activities of the complex were evaluated by minimum inhibitory concentration and the results showed that the complex exhibited moderate activities against gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*) and molds (*Aspergillus niger, Penicillium citrinum*).

---

* Corresponding authors. Tel.: +92 333 5248570 (S. Ahmad). Tel.: +34 868 88 7489; fax: +34 868 88 4149 (A. Espinosa). Tel.: +34 868 88 74 55; fax: +34 868 88 4148 (J. Ruiz).
E-mail addresses: saeed_a786@hotmail.com (S. Ahmad), artuesp@um.es (A. Espinosa), jruiz@um.es (J. Ruiz).
URLs: http://www.um.es/multipropchem/artuesp (A. Espinosa), http://www.um.es/qcqo/jruiz.htm (J. Ruiz).

http://dx.doi.org/10.1016/j.molstruc.2014.12.076
0022-2860/

Introduction

Platinum compounds represent the most effective and widely used anticancer drugs [1,2]. However, their use is restricted because of the severe side effects and due to drug resistance caused by the platinum binding to biological thiolate molecules [2–4]. Thiourea and its derivatives are among such S-donor ligands that are used as chemoprotectants against nephrotoxicity after cisplatin treatment [4,5]. Several platinum(II) complexes of thioureas are also known to exhibit antibacterial and antitumor activity [6]. In addition, $[Pt(thiourea)_4]^{+2}$ complexes have been found suitable as molecular building blocks in the synthesis of hydrogen bonding networks [7]. Considering the above mentioned facts crystal structures of several platinum(II) complexes of thioureas have been reported in the literature [7,8]. The coordination of soft platinum(II) ion to thioureas in these compounds occurs through the softer sulfur atom [7,8].

In this paper, we present the crystal structure and biological properties of a new platinum(II) complex with tetramethylthiourea (Tmtu) and cyanide as ligands, $[Pt(Tmtu)_4][Pt(CN)_4]\cdot 4H_2O$ (**1**), together with experimental and theoretical support for explaining its formation. The spectroscopic data and theoretical structure of another new complex, $[Pt_2(CN)_3(Tmtu)_3]CN$ (**3**), is also presented.

Results and discussion

Synthesis and spectroscopic characterization

The sequential reaction of $K_2[PtCl_4]$ with KCN and Tmtu in a 1:2:2 M ratio resulted in a final product **1** of empirical composition $Pt(Tmtu)_2(CN)_2{\cdot}2H_2O$ (Scheme 1). In the IR spectrum of **1** characteristic bands for coordinated Tmtu were observed: ν(C=S) at 607 cm^{-1} and ν(C—N) at 1561 cm^{-1}. For the free Tmtu these bands were observed at 622 and 1491 cm^{-1}, respectively [9]. The cyanide CN stretching frequency at 2128 cm^{-1} is close to that observed for the $[Pt(CN)_4]^{2-}$ ion [10]. The ν(O—H) vibration appeared at 3400 cm^{-1} showing the presence of hydrogen bonded water molecules in the complex.

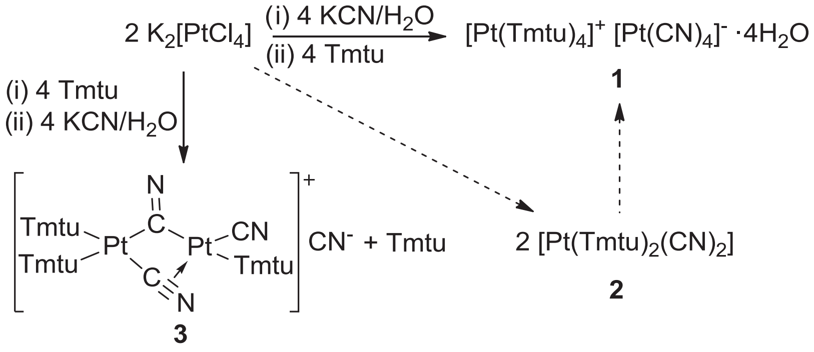
The ^1H NMR spectrum of **1** displayed a downfield shift in the N—CH_3 resonance signals compared to uncomplexed Tmtu (3.21 ppm vs 3.08 ppm), which is related to an increase in π electron density at the C—N bond upon coordination. In the ^{13}C NMR spectrum of **1**, the main change brought by complexation is the shifting of the C=S resonance towards the upfield region (180.80, 192.78 *vs* 193.42 ppm in Tmtu). The appearance of two resonances could be tentatively explained by considering equilibration of the complex in solution with some other species such as $[Pt(Tmtu)_2(CN)_2]$, **2** (*vide infra*). The N—CH_3 resonances appeared at 43.90 and 42.77 ppm (42.05 ppm for the free ligand). The observation of the cyanide carbon atom signal at 121.79 ppm confirms the coordination of cyanide.

In order to check the plausible intermediacy of mononuclear complex **2**, the reaction was also carried out in the inverse order for the addition of reagents. Under these conditions complex **2** was not detected but the same product **1** was obtained together with traces of a new bridged dinuclear complex **3** (Scheme 1). This compound displays three well resolved peaks in the IR spectrum at 2122, 2134 and 2181 cm^{-1}, as well as a broad weak signal centered around 2250 cm^{-1}, which are attributable to the four different cyanide groups and assigned by comparison to data from theoretical calculations (*vide infra*), and a intense broad signal centered at 1563 cm^{-1} due to the C—N stretching. In the ^1H NMR spectrum of **3** a complex signal in the range 3.25–3.40 ppm was attributed to coordinated Tmtu moieties, whereas the remaining singlet at 3.08 ppm was assigned to an uncomplexed Tmtu molecule and confirmed by increase of the signal upon addition of that reagent. The appearance of four signals in the C=S region of the ^{13}C NMR spectrum at 194.1, 186.7, 186.3 and 184.6 ppm, and four N—CH_3 resonances at 44.5, 44.4, 44.3 and 43.2 ppm (only two peaks attributable to CN resonances can be scarcely recognized above noise at 125.1 and 123.3 ppm) provides additional evidence supporting the proposed structure of complex **3**. Furthermore, the HRMS (positive mode) confirms the existence of the $(M+1)^+$ ion for **3** (*m/z* = 891.1653 a.m.u.) with isotopic pattern in perfect agreement with the calculated one (see Fig. S2).

X-ray structure description

The molecular structure of compound **1** is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. The structure of **1** consists of a divalent cationic complex, $[Pt(Tmtu)_4]^{2+}$ and two crystallographically independent $[Pt(CN)_4]^{2-}$ anions (A and B), each of which resides on a center of symmetry (thus there are two half anions in the asymmetric unit). In $[Pt(CN)_4]^{2-}$, the PtC_4 coordination unit is strictly planar due to an inversion center at the Pt atom for both anions A and B. In $[Pt(Tmtu)_4]^{2+}$, the platinum atom lies within the S_4 plane (deviation ~0.001 Å). The bond angles around Pt^{2+} (the average *cis* and *trans* angles being 90.29° and 171.9° respectively) show some distortion from the regular square planar geometry due to steric constraints of the large Tmtu molecules. The Pt—C≡N moiety is nearly linear with an average bond angle of 177.8°. The carbon atoms in the N—C=S moieties of the ligands are sp^2-hybridized. The Pt—S, Pt—C and other bond distances are in accordance with those reported for related complexes [11]. Most likely, the existence of the complex in the ionic form, $[Pt(Tmtu)_4]^{2+}[Pt(CN)_4]^{2-}$ is due to the high stability of $[Pt(CN)_4]^{2-}$ complex ion in the solid state.

Four O atoms corresponding to water molecules of crystallization were found in the cell, but their hydrogen atoms could not



Scheme 1. Synthesis of complexes **1** and **3** and possible intermediate **2**.