

Inorganica Chimica Acta 333 (2002) 93-99



www.elsevier.com/locate/ica

# The X-ray structure and spectroscopy of platinum(II) complexes with 1,2,4-triazolo[1,5-*a*]pyrimidines and dimethylsulfoxide

Edward Szłyk<sup>a</sup>, Iwona Łakomska<sup>a,\*</sup>, Andrzej Surdykowski<sup>a</sup>, Tadeusz Głowiak<sup>b</sup>, Leszek Pazderski<sup>a</sup>, Jerzy Sitkowski<sup>c</sup>, Lech Kozerski<sup>c</sup>

> <sup>a</sup> Faculty of Chemistry, Nicholas Copernicus University, Gagarina 7, 87-100 Toruń, Poland <sup>b</sup> Institute of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wrocław, Poland <sup>c</sup> Drug Institute, Chelmska 30/34, 00-725 Warsaw, Poland

> > Received 18 October 2001; accepted 14 January 2002

# Abstract

Platinum(II) complexes with 1,2,4-triazolo[1,5-*a*]pyrimidines of general formula *trans*-[PtCl<sub>2</sub>(dmso)(L)], where L = 1,2,4-triazolo[1,5-*a*]pyrimidine (tp), 5,7-dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidine (dmtp), 5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (dptp), 5,7-ditertbutyl-1,2,4-triazolo[1,5-*a*]pyrimidine (dbtp) have been prepared by direct reaction between *cis*-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] and respective 1,2,4-triazolo[1,5-*a*]pyrimidine in molar ratio M:L = 1:1. All new platinum(II) compounds were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, <sup>195</sup>Pt NMR and IR. Significant <sup>15</sup>N NMR upfield shifts (75–87 ppm) were observed for N(3) atom indicating this nitrogen atom as a coordination site. Crystal structure of *trans*-[PtCl<sub>2</sub>(dmso)(dmtp)] (**2**) has been determinated. The molecular structure indicates that Pt(II) ion has the square-planar geometry with N(3) bonded dmtp, S-bonded dimethylsulfoxide and two *trans* chloride anions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pt(II) complexes; 1,2,4-triazolo[1,5-a]pyrimidine; NMR; Crystal structures; <sup>15</sup>N NMR; IR

# 1. Introduction

The chemistry of heterocycles with a purine ring skeleton is of wide interest [1]. Usually, such ligands have multiple coordination sites, hence different varieties of coordination modes are possible. This prompted us to study 1,2,4-triazolo[1,5-*a*]pyrimidine, a ligand whose skeleton differs from the purine ring system in having a pyrimidine atom in a bridgehead position with disappearance of the acidic H-proton of the five-membered ring. The figure below (Fig. 1) compares these two bicyclic systems. These triazolopyrimidines have also influence on the behavior of other auxiliary ligands, either by electronic or steric reasons, giving rise in some cases to compounds with interesting metal-metal interaction [2]. In addition, the transition metal

complexes with 1,2,4-triazolo[1,5-*a*]pyrimidines can be related to a metal-ligand interactions similar to one observed in biological systems [3]. The 1,2,4-triazole derived ligands show a remarkable resemblance to imidazole, although some differences appear in the coordination behavior of these ligands [4]. Studies on the naturally-occurring bases (guanine, adenine) have revealed that the purine prefers the imidazole N(9) atom for coordination, however ligation via N(7) atom is also observed [5]. In order to better elucidate the influence of steric effects on the coordination sites, we have characterized some metal complexes using 5,7-disubstituted-1,2,4-triazolo[1,5-*a*]pyrimidines.

Reported studies of triazolopyrimidines complexes with mono-, di- and multinuclear structures exhibited the influence of the central ion, inorganic anions and heterocycle ligand on the complex geometry [6–10]. However, platinum(II) complexes with triazolopyrimidines have been studied to a much less extent. The chemistry of platinum group metals and 1,2,4-triazolo[1,5-*a*]pyrimidine ligands has been dominated by

<sup>\*</sup> Corresponding author. Tel.: +48-56-611 4302; fax: +48-56-654 2477.

E-mail address: dziubek@cc.uni.torun.pl (I. Lakomska).



Fig. 1. IUPAC numbering of (a) 5,7-disubstituted-1,2,4-triazolo[1,5-a]pyrimidine, where R-H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, C(CH<sub>3</sub>)<sub>3</sub>, and (b) adenine molecule.

Pt(II) [6,11,12], Pd(II) [13,14] and Ru(III) [15] compounds, because these complexes often show biological activity. Some coordination compounds of Pt(II), Pd(II) and Ru(III) were described: cis-[Pt(II)(HmtpO)<sub>2</sub>- $(NH_3)_2 (NO_3)_2 \cdot 2H_2O_1$  $[Pt(II)(dmtp)_4][Pt(IV)(SCN)_6],$ trans-[Pd(II)(dmtp)<sub>2</sub>Br<sub>2</sub>]·CH<sub>3</sub>OH, mer-[Ru(III)(dmtp)<sub>2</sub>- $Cl_3(H_2O)$ ]·H<sub>2</sub>O and mer-[Ru(III)(2-amino-dmtp)<sub>2</sub>- $Cl_3(H_2O)$ ]·H<sub>2</sub>O [6,11,13,15,16], but the high antitumor activity was exhibited only for cis-[Pt(II)(HmtpO- $N^{3}_{2}Cl_{2} \cdot 2H_{2}O$  [12]. The intention of our research is to find new platinum(II) compounds which show similar activity to cisplatin and carboplatin, but have an additional functional group where they may be linked to carrier substances. For our study, we choose triazolopyrimidines, which have a similar structure to purine ring and dimethylsulfoxide as labilizing ligand. It is a first report of mixed Pt(II) complexes with 1,2,4triazolo[1,5-a]pyrimidines and dimethylsulfoxide. In this paper we study four platinum(II) complexes with unsubstituted tp and its 5,7-substituted derivatives (dmtp, dptp, dbtp): trans-[PtCl<sub>2</sub>(dmso)(tp)] (1), trans- $[PtCl_2(dmso)(dmtp)]$  (2), trans- $[PtCl_2(dmso)(dptp)]$  (3) and trans-[PtCl<sub>2</sub>(dmso)(dbtp)] (4).

# 2. Experimental

## 2.1. Materials

Dipotassium tetrachloroplatinum(II), 1,2,4-triazolo[1,5-*a*]pyrimidine and dimethylsulfoxide, 3-amino-1,2,4-triazole (98%), 2,4-pentanedione (99%) and 1,3diphenyl-1,3-propanedione (99%), 2,2,6,6-tetramethyl-3,5-heptanedione (98%), were purchased from Aldrich, whereas the inorganic salts of analytical grade from POCh Gliwice (Poland).

5,7-Disubsituted derivatives of 1,2,4-triazolo[1,5-*a*]pyrimidines were prepared according to the Bülow and Haas method [17] by the reaction of 3-amino-1,2,4triazole with 2,4-pentanedione for dmtp, 1,3-diphenyl-1,3-propanedione for dptp and 2,2,6,6-tetramethyl-3,5heptanedione for dbtp [18].

## 2.2. Instrumentation

IR spectra were measured with a Perkin–Elmer Spectrum 2000 FT IR spectrometer, using KBr (400–4000 cm<sup>-1</sup>) and polyethylene discs (100–400 cm<sup>-1</sup>). <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, <sup>195</sup>Pt NMR spectra were performed on a Varian INOVA 500 spectrometer equipped with inverse Nalorac Z gradient shielded probe. <sup>15</sup>N NMR was detected by 2D <sup>1</sup>H–<sup>15</sup>N gradient selected Heteronuclear Multiple Quantum Correlation (HMQC) in the absolute value mode. <sup>195</sup>Pt NMR of Pt(II) species were measured by 1D technique optimized for fast relaxing nuclei (acquisition time 10 ms, relaxation delay 10 ms, flip angle 20°, spectral width 100 kHz). The solvent was d<sub>7</sub>-dmf, the concentration of samples 0.05 M, the temperature 298 K. The reference standard was TMS for <sup>1</sup>H and <sup>13</sup>C; CH<sub>3</sub>NO<sub>2</sub> for <sup>15</sup>N and K<sub>2</sub>PtCl<sub>6</sub> for <sup>195</sup>Pt.

C, H, N were determined by semimicroanalysis whereas platinum was determinated by spectrophotometric method on Specord M40 Carl Zeiss Jena ( $\lambda = 400$  nm).

# 2.3. Syntheses

The compound cis-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] was prepared by the known method [19].

The new platinum(II) complexes were prepared by reaction of *cis*-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] with 1,2,4-triazolo[1,5-*a*]-pyrimidines (tp, dmtp, dptp) in molar ratio M:L = 1:1 in ethanol solution. The details of particular syntheses are given below.

# 2.3.1. $trans-[PtCl_2(dmso)(tp)]$ (1)

A suspension of *cis*-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] (0.201g; 0.5 mmol) in 20 ml of ethanol was treated with the stoichiometric amount of tp (0.060 g; 0.5 mmol) in 10 ml of the same solution and the reaction mixture stirred at room temperature (r.t.) for 1 h. The yellow precipitate was filtered, washed with ethanol, acetone, diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. Yield 0.197 g (85%). *Anal.* Found: C, 18.0; H, 2.2; N, 12.1, Pt 39.8%. Calc. for C<sub>7</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>4</sub>OSPt: C, 18.1; H, 2.2; N, 12.1; Pt, 42.0%. The melting point (m.p.) of the complexes is > 250 °C (dec.).

## 2.3.2. $trans - [PtCl_2(dmso)(dmtp)]$ (2)

A suspension of *cis*-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] (0.201g; 0.5 mmol) in 20 ml of ethanol was treated with the stoichiometric amount of dmtp (0.070 g; 0.5 mmol) in 10 ml of the same solution. The reaction mixture was stirred at r.t. for 30 min. The yellow precipitate was filtered, washed with ethanol, acetone, diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. Yield 0.196 g (80%). *Anal.* Found: C, 22.4; H, 2.9; N, 11.4; Pt, 39.4%. Calc. for C<sub>9</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>4</sub>OSPt: C, 22.0; H, 2.9; N, 11.4; Pt, 39.6%. The m.p. of the complex is > 250 °C (dec.).

### 2.3.3. $trans-[PtCl_2(dmso)(dptp)]$ (3)

A suspension of *cis*-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] (0.102 g; 0.2 mmol) in 20 ml of ethanol was treated with the stoichiometric amount of dptp (0.048 g; 0.2 mmol) in the ethanol. The reaction mixture was heated by stirring at 50 °C, for 2 h. The yellow precipitate was filtered directly from hot solution, washed with boiling ethanol and then dried in vacuum over P<sub>2</sub>O<sub>5</sub>. Yield 0.111 g (75%). *Anal.* Found: C, 36.8; H, 3.0; N, 8.8; Pt 31.5%. Calc. for C<sub>19</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>4</sub>OSPt: C, 37.0; H, 2.9; N, 9.1; Pt 31.6%. The m.p. of the complexes is > 250 °C (dec.).

#### 2.3.4. trans- $[PtCl_2(dmso)(dbtp)]$ (4)

A suspension of *cis*-[PtCl<sub>2</sub>(dmso)<sub>2</sub>] (0.201 g; 0.5 mmol) in 20 ml of ethanol was treated with the stoichiometric amount of dbtp (0.116 g; 0.5 mmol) in 10 ml of the same solution. The reaction mixture was stirred at r.t. for 2 h. The yellow precipitate was filtered, washed with ethanol, acetone, diethyl ether and dried in vacuum over P<sub>2</sub>O<sub>5</sub> 0.202 g (70%). *Anal.* Found: C, 31.2; H, 4.7; N, 9.3; Pt, 33.5%. Calc. for C<sub>15</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>OSPt: C, 31.2; H, 4.6; N, 9.7; Pt, 33.8%. The m.p. of the complexes is > 250 °C (dec.).

# 2.4. Crystal structure determination of (2)

The crystals of 2 were obtained by slow crystallization from ethanol-hexane-CH<sub>2</sub>Cl<sub>2</sub> solution. The X-ray data were collected on a Kuma KM4 CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation,  $\lambda =$ 0.71069 Å using  $-2\theta$  method. No absorption correction was applied. Data reduction on analysis was carried out with the Kuma Diffraction programs. The structure was solved by direct methods (program SHELXS-97) [20] and refined by the full-matrix least-squares method on all  $F^2$ data using the SHELXL-97 programs [21]. Non-hydrogen atoms were refined with anisotropic-thermal parameters. Hydrogen atoms were included from geometry of molecule. During refinement, they were rated as rigid groups with fixed interatomic distances. The atomic scattering factors were taken from International Tables for Crystallography [22]. The crystal data of compound 2 are listed in Table 1.

## 3. Results and discussion

## 3.1. Discussion of the crystal structure

The crystal structure of **2** consists of monomeric  $[PtCl_2(dmso)(dmtp)]$  units. The projection of the molecule with the atomic numbering scheme is presented in Fig. 2, whereas the relevant bond distances and bond angles are listed in Table 2.

The Pt atom has the square-planar geometry slightly distorted towards tetrahedron. The deviations from the

Table 1 Crystallographic date for complex **2** 

Empirical formula	$C_9H_{14}Cl_2N_4OPtS$
M	492.29
Crystal system	orthorhombic
Temperature	100(1) K
Space group	Pbca
a (Å)	10.542(2)
b (Å)	12.661(3)
<i>c</i> (Å)	21.334(4)
V (Å <sup>3</sup> )	2847.5(10)
Ζ	8
Density (calculated) (mg $m^{-3}$ )	2.297
$\mu  ({\rm mm}^{-1})$	10.370
F(000)	1856
Crystal size (mm)	$0.10 \times 0.10 \times 0.15$
$\theta$ Range for data collection (°)	3.2-25.0
Index ranges	$-12 \le h \le 12, -15 \le k \le 9,$
-	$-25 \le l \le 25$
Reflections collected	14031
Reflections unique	2480 $[R_{int} = 0.064]$
Goodness-of-fit on $F^2$	1.173
Data/parameters	2411/167
Final $R1$ , $wR2$ indices $[I > 2\sigma(I)]$	0.051, 0.14
All data	0.052, 0.14
Largest difference peak and hole (e $Å^{-3}$ )	4.02 and -2.91



Fig. 2. The ORTEP [23] drawing of the  $[PtCl_2(dmso)(dmtp)]$  (2) molecule.

best weighted plane of the ligating atoms are: Cl(1), -0.0545(15); Cl(2), -0.0563(15); S, 0.0515(14); N(3), 0.0593(16) and Pt, 0.0089(15) Å. The dmtp ligand is monodentately bonded via N(3). The relatively high trans effect of the sulfur donor atom results in elongation of the Pt-N(3) distance [2.048(5) Å in (2)] which is longer than the ones in cis-[PtCl<sub>2</sub>(dmtp)<sub>2</sub>] [2.020(3) and 2.024(3) Å] [24]. In  $[Pt(dmtp)_4][Pt(SCN)_6]$  the Pt-N(3)distances have been even shorter [1.97(3) and 2.03(3) Å] but the data have been of low accuracy [6]. The Pt-S distance of 2.221(2) Å is similar to the reported for other Pt-dmso complexes [25]. Sulfur atoms in dimethylsulfoxide are in an approximate tetrahedral environment although the biggest deviation has been observed for the Pt-S-O  $(114.7(2)^{\circ})$  and C-S-C  $(100.1(3)^{\circ})$  angles. Chloride ions are in trans position, the Pt-Cl distances

Table 2 Selected bond lengths (Å) and angles (°) for  ${\bf 2}$ 

Bond lengths			
Pt-N(3)	2.048(5)	N(3) - C(3A)	1.339(8)
Pt-S	2.221(2)	N(3) - C(2)	1.360(8)
Pt-Cl(2)	2.295(2)	N(4)-C(3A)	1.332(8)
Pt-Cl(1)	2.303(2)	N(4) - C(5)	1.346(8)
S-O(1)	1.470(5)	N(8)-C(3A)	1.352(8)
S-C(11)	1.765(6)	N(8) - C(7)	1.381(8)
S-C(12)	1.780(8)	C(5) - C(6)	1.417(10)
N(1)-C(2)	1.322(9)	C(5) - C(9)	1.504(9)
N(1)-N(8)	1.379(8)	C(6) - C(7)	1.373(10)
		C(7) - C(10)	1.483(9)
Bond angles			
N(3)-Pt-S	176.9(2)	C(3A) - N(8) - C(7)	122.7(6)
N(3)-Pt-Cl(2)	89.2(2)	N(1)-N(8)-C(7)	125.7(6)
S-Pt-Cl(2)	88.95(6)	N(1)-C(2)-N(3)	115.0(6)
N(3)-Pt-Cl(1)	87.63(15)	N(4) - C(3A) - N(3)	128.1(6)
S-Pt-Cl(1)	94.33(6)	N(4) - C(3A) - N(8)	124.3(6)
Cl(2)-Pt-Cl(1)	175.46(5)	N(3)-C(3A)-N(8)	107.5(5)
O(1) - S - C(11)	108.7(3)	N(4) - C(5) - C(6)	122.4(6)
O(1) - S - C(12)	109.1(4)	N(4)-C(5)-C(9)	117.6(6)
C(11) - S - C(12)	100.1(3)	C(6) - C(5) - C(9)	119.9(6)
C(2)-N(1)-N(8)	101.4(5)	C(7) - C(6) - C(5)	121.2(6)
C(3A) - N(3) - C(2)	104.6(5)	C(6)-C(7)-N(8)	114.1(6)
C(3A) - N(4) - C(5)	115.3(5)	C(6)-C(7)-C(10)	127.2(6)
C(3A) - N(8) - N(1)	111.5(5)	N(8)-C(7)-C(10)	118.7(6)

being 2.295(2) and 2.303(2) Å as expected for this type of compounds. The analysis of the dmtp ligand planarity data indicates that the fused-ring system is essentially planar. The nine atoms comprising the triazolopyrimidine core have the rms deviation of 0.014 Å from the least-squares plane. This ring system is slightly bent along the N(8)-C(3a) bond as indicated by the interplanar angle of  $2.0(3)^{\circ}$  between the planes calculated for six atoms of the pyrimidine ring and five atoms of the triazole moiety. The mean plane through the nineframework of the dmtp ligand makes the dihedral angle with the mean basal coordination plane of  $61.7(1)^{\circ}$ . The bond distances in the coordinated ligand are similar to the ones found in solvated dmtp [26]. In contrast the bond angles within the imidazole ring exhibit important differences. They are larger at N(3)  $[104.6(5)^{\circ}]$  and smaller at C(2)  $[115.0(6)^{\circ}]$  and C(3a)  $[107.5(5)^{\circ}]$  as compared with the neutral ligand, 102.2(3), 117.6(4) and  $109.5(3)^{\circ}$ , respectively.

Previous crystallographic studies carried out on metal-dmtp complexes have indicated that the N(3) atom in the unidentate form is the most preferred binding site. This coordination mode was found for Pt(II) [6], Pd(II) [13,14], Cd(II) [27], Hg(II) [28], Co(II) [28], Cu(II) [29], Ni(II) [30], Zn(II) [31], and Ru(III) [15] complexes. The N(3), N(4) bridging bidentate coordination has been found only in a cluster [Cu<sub>4</sub>(dmtp)<sub>4</sub>-Cl<sub>2</sub>][Cu<sub>2</sub>Cl<sub>4</sub>] [32] and in some dimeric Ag(I)-dmtp compounds [33]. This proves that dmtp can be a good

model, which exhibits the one preferred site for coordination to metal ion in biological system.

# 3.2. NMR spectroscopy

The <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR spectra of the ligands were reported by many authors, however, the data concerned CDCl<sub>3</sub> or dmso-d<sub>6</sub> solutions [18,34–45]. During this work we had to perform all the measurements in  $dmf-d_7$ , due to insolubility or decomposition of the complexes in the former solvents. The assignment of the signals for both ligands and complexes was based on heteronuclear correlation methods (HETCOR), analogous to those described by us in earlier reports [14,18,45]. In the case of dptp complex, we have observed the two forms 3a and 3b, differing in their NMR spectra, the former existing shortly after dissolving the sample in d<sub>7</sub>-dmf and the latter appearing after 24 h. Probably we observed *trans*  $\rightarrow$  *cis* isomerisation under the influence of dmf alone. Isomerization catalyzed by pyridine and another nucleophilic agent is a fairly common phenomenon and occurs either via pseudorotation of fivecoordination intermediate or through a consecutive displacement of ligands [46,47].

The <sup>1</sup>H and <sup>13</sup>C NMR data of the studied complexes are listed in Table 3.

For 1–4 the chemical shifts changes pattern is very clear. The coordination of triazolopyrimidine molecules by Pt(II) ions results in the downfield shift of H(2) and H(6) resonances (0.3-0.9 ppm). The carbons adjacent to N(3) coordination site, i.e. C(2) and C(3a) are shifted upfield (1.5-3.7 ppm) whereas the others, C(5), C(6) and C(7)-downfield (2-4.4 ppm). The shielding of the carbon atoms, adjacent to the coordination site N(3), as well as the deshielding of the other carbons and the protons inside the heterocyclic ring was already described by us for some Pd(II) chloride complexes with tp and its derivatives [14].

In the <sup>1</sup>H NMR spectra of 1–4, we also observe the signal of CH<sub>3</sub> groups of dmso molecules. Its  $\delta$  value, 3.50–3.56 ppm, is typical for those sulfur-bonded ligands [48]. In the case of 1 and 4 it appears as a singlet and no <sup>195</sup>Pt{<sup>1</sup>H} spin–spin interaction has been detected whereas for 2 and 3 the <sup>195</sup>Pt{<sup>1</sup>H} coupling was observed. A single CH<sub>3</sub> resonance with <sup>195</sup>Pt satellites indicates the absence of the detectable ligand dissociation and retention of the S-bonded structure in this solvent. The calculated values of the <sup>3</sup>J<sub>Pt-H</sub> coupling constants, being 10.3 Hz for 2 and 9.9 Hz for 3 are lower than for analogous coordination compounds with other heterocycle ligands (thiazole [49] and quinoline [50]).

The <sup>15</sup>N and <sup>195</sup>Pt NMR data for the ligands and complexes are collected in Table 4.

During this work, we have measured <sup>15</sup>N-<sup>1</sup>H HET-COR spectra for all discussed ligands and new platinum(II) complexes, assigning all <sup>15</sup>N resonances.

97

Table 3 <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts ( $\delta$ ) of platinum(II) complexes in dmf-d<sub>7</sub> (coordination shifts in parentheses)

Compound	H(2)	H(6)	C(2)	C(3a)	C(5)	C(6)	C(7)
1 2 3a 3b 4	$\begin{array}{c} 9.17 \ (+0.45) \\ 9.00 \ (+0.41) \\ 9.08 \ (+0.59) \\ 9.17 \ (+0.68) \\ 9.11 \ (+0.47) \end{array}$	7.79 (+0.32) 7.53 (+0.34) 8.48 (+0.87) 8.50 (+0.89) 7.54 (+0.27)	155.1 (-1.6) 153.7 (-2.2) 154.4 (-2.4) 155.0 (-1.8) 153.8 (-1.5)	152.5 (-3.5) 152.3 (-3.5) 153.5 (-3.6) 153.4 (-3.7) 152.8 (-3.7) 152.8 (-3.7)	159.7 (+3.6) 169.5 (+4.1) 164.4 (+2.7) 164.7 (+3.3) 180.0 (+4.4)	114.7 (+3.1) 114.6 (+3.1) 110.3 (+2.8) 110.6 (+3.1) 108.2 (+3.6)	140.0 (+2.0) 150.2 (+2.2) 150.3 (+1.7) 150.4 (+1.8) 159.7 (+1.8) 159.7 (+1.8)

Table 4 <sup>15</sup>N NMR and <sup>195</sup>Pt chemical shifts ( $\delta$ ) of platinum(II) complexes in d<sub>7</sub>-dmf (coordination shifts in parentheses)

Compound	N(1)	N(3)	N(4)	N(8)	Pt <sup>a</sup>
1	-105.9(+0.1)	-236.2 (-84.9)	-108.6 (-5.4)	-157.7 (-3.4)	-2953 (+523)
2	-110.9(+0.1)	-228.6(-74.7)	-118.6(-2.8)	-157.6 (-2.3)	-3008(+468)
3a	-110.6(+0.1)	-227.8 (-77.1)	-125.8 (-5.4)	-161.9(-2.6)	-2954 (+522)
3b	-111.0(-0.5)	-237.4(-86.7)	-128.5(-8.1)	-163.3(-4.0)	-3066(+410)
4	-108.6 (-1.0)	-238.4 (-85.3)	-122.0 (-6.2)	-162.2 (-3.5)	-2955 (+521)

<sup>a</sup> For <sup>195</sup>Pt the value in parentheses is the shift related to starting material *cis*-[Pt(dmso)<sub>2</sub>Cl<sub>2</sub>] ( $\delta = -3476$  ppm).

In the case of 1–4 the Pt(II) coordination affects most significantly N(3) signal, shifting it upfield 74.7–86.7 ppm. Such a diamagnetic shift unambiguously indicates that the complexation occurs via N(3). The absolute values of the coordination shifts are smaller than for Pd(II) (78–90 ppm) complexes [14]. The increased shielding of the Pt(II) coordinated nitrogen nucleus is, most likely, the result of the decrease of the absolute value of the paramagnetic term in its <sup>15</sup>N NMR shielding constant. Such a phenomenon was already reported for several Pt(II) complexes with ammonia, the coordination shifts varying from -70 to -90 ppm.

Single <sup>195</sup>Pt resonance appeared in the range (-2953)to -3066 ppm). Such values of <sup>195</sup>Pt chemical shifts are typical for Pt(II) complexes with N-donor heteroaromatic compounds [51-55]. Spectra of the complexes under discussion exhibit <sup>195</sup>Pt resonances shifted downfield 410–523 ppm in relation to the starting platinum complex, cis-[PtCl<sub>2</sub>(dmso)<sub>2</sub>]. Downfield coordination shift can be explained by the charge shift from ligand to the metal center caused by Pt-N bond formation. The majority of 5,7-disubsituted derivatives of 1,2,4triazolo[1,5-a]pyrimidines revealed downfield shift at <sup>195</sup>Pt resonance in relation to their unsubstituted counterpart. This feature is in favor of the smaller donor strength of the unsubstituted heterocycles. Presented complexes generally exhibit a higher downfield shift of the platinum signals than that observed for complexes with pyridine and non-bulky pyridines [56]. The <sup>195</sup>Pt signals of Pt(II) complexes 1-4 have been detected as broad singlets, their half-line widths being approximately 200-420 Hz. Such values are relatively high,

comparing to those found for  $[PtCl_4]^{2-}$  ions (ca. 110 Hz) [57], which can be explained, most likely, by the quadrupolar interactions between <sup>195</sup>Pt and <sup>14</sup>N nuclei.

## 3.3. Infrared studies

Characteristic bands of the whole triazolopyrimidine ring skeletal vibrations appeared at 1619 (1), 1633 (2), 1618 (3) and 1618 cm<sup>-1</sup> (4), whereas those of the pyrimidine ring at 1565 (1), 1555 (2), 1555 (3), 1543  $\mathrm{cm}^{-1}$  (4). In the spectra of free ligands the former band was found at 1620 (tp), 1633 (dmtp), 1611 (dptp), 1615  $cm^{-1}$  (dbtp) and the latter one at 1553 (tp), 1550 (dmtp), 1539 (dptp), 1530 cm<sup>-1</sup> (dbtp) [45]. The two most characteristic bands, assigned previously by us as triazolopyrimidine ring skeletal vibration and pyrimidine ring skeletal vibration are shifted not more than 13  $cm^{-1}$ . Similar effect has already been observed for different complexes with tp, dmtp or dptp, where the N(3) coordination occurred. The strong absorption bands at 1142-1147 cm<sup>-1</sup> range indicate S-bonded dmso, as expected for this typical soft coordination center [48,49,58]. Far-IR spectroscopy of 1-4 has exhibited one new absorption band of high intensity in a narrow range 338-347 cm<sup>-1</sup>. Its position is similar to that found for some chloride complexes of Pt(II) with thiazole (347 cm<sup>-1</sup>) [49], mercaptoimidazole [59] and mercaptopyrimidine [59] derives, most likely, from a Pt-Cl stretching vibration. The IR spectra contain also the bands at 289-282 cm<sup>-1</sup>, those can be assigned to Pt-N stretching modes [59,60].

## 4. Conclusion

The present study describes a series of *trans*-dichloro complexes of Pt(II) with dimethylsulfoxide and 1,2,4-triazolo[1,5-*a*]pyrimidines. The platinum(II) complexation results in a large upfield shift of <sup>15</sup>N NMR signals of coordinated nitrogens (ca. 75–87 ppm) and proves that coordination of investigated 1,2,4-triazolo[1,5-*a*]pyrimidines occurs via N(3). The observed coordination mode via N(3) may be regarded as respective for these heterocycles and analogous to N(9) complexion purines. The crystal structure of **2** indicates that Pt(II) ion has the square-planar geometry with N(3) bonded dmtp, S-bonded dimethylsulfoxide and two *trans* chloride anions.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 158067. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

#### References

- [1] J.G. Haasnoot, Coord. Chem. Rev. 200-202 (2000) 1131.
- [2] J.A.R. Navarro, M.A. Romero, J.M. Salas, M. Quirós, E.R.T. Tiekink, Inorg. Chem. 36 (1997) 4988.
- [3] J.A. Tainer, E.D. Getzoff, K.M. Beem, J.S. Richardson, D.C. Richardson, J. Mol. Biol. 160 (1982) 181.
- [4] J.G. Haasnoot, W.L. Groeneveld, Z. Naturfosch., Teil B 32 (1977) 533.
- [5] R. Tauler, M.J.A. Rainer, B.M. Rode, Inorg. Chim. Acta 123 (1986) 75.
- [6] M. Biagini-Cingi, A.M. Manotti-Lanfredi, A. Tiripicchio, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 72 (1983) 81.
- [7] A. Grodzicki, E. Szłyk, A. Wojtczak, G. Wrzeszcz, L. Pazderski, T. Musioł, Polyhedron 18 (1998) 519.
- [8] G.A. van Albada, R.A.G. de Graff, J.G. Haasnoot, J. Schild, J. Reedijk, Acta Crystallogr., Sect. C 47 (1991) 946.
- [9] M. Biagini-Cingi, A.M. Manotti-Lanfredi, A. Tiripicchio, A. Cornelissen, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 129 (1987) 217.
- [10] J.M. Salas, M.A. Romero, M.P. Sánches, M. Quirós, Coord. Chem. Rev. 195 (1999) 1119.
- [11] J.A.R. Navarro, M.A. Romero, J.M. Salas, M. Quirós, Inorg. Chem. 36 (1997) 3277.
- [12] J.A.R. Navarro, J.M. Salas, M.A. Romero, R. Vilaplana, F. Gozález-Vilchez, R. Faure, J. Med. Chem. 41 (1998) 332.
- [13] R. Hage, R.A.G. Graaff, J.G. Haasnoot, K. Kieler, J. Reedijk, Acta Crystallogr., Sect. C 46 (1990) 2349.
- [14] E. Szłyk, A. Grodzicki, L. Pazderski, A. Wojtczak, J. Chatłas, G. Wrzeszcz, J. Sitkowski, B. Kamieński, J. Chem. Soc., Dalton Trans. (2000) 867.

- [15] A.H. Velders, L. Pazderski, F. Ugozzoli, M. Biagini-Cingi, A.M. Manotti-Lanfredi, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 273 (1998) 259.
- [16] J.A.R. Navarro, M.A. Romero, J.M. Salas, M. Quiros, Inorg. Chem. 36 (1997) 3277.
- [17] C. Bülow, K. Haas, Ber. Dtsch. Chem. Ges. 42 (1909) 4638.
- [18] A. Grodzicki, E. Szłyk, L. Pazderski, A. Goliński, Magn. Res. Chem. 34 (1996) 725.
- [19] J.H. Price, A.S. Williamson, R.S. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280.
- [20] G.M. Sheldrick, Acta Crystallogr., Sect. B 37 (1990) 467.
- [21] G.M. Sheldrick, SHELXL-93, program for refinement of crystal structures, University of Gottingen, Germany, 1994.
- [22] International Tables for Crystallography, Kluwer Academic Publishers, Dordrecht, 1992.
- [23] C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- [24] J. Reedijk, K. Schmith, I. Łakomska, unpublished results.
- [25] F.H. Allen, O. Kennard, R. Taylor, Acc. Chem. Res. 16 (1983) 146.
- [26] J.M. Salas, A. Rahmani, M.A. Romero, M. Quiros, E.R.T. Tiekink, J. Chem. Crystallogr. 24 (1994) 669.
- [27] J. Dillen, A.T.H. Lenstra, J.G. Hasnoot, J. Reedijk, Polyhedron 2 (1983) 195.
- [28] M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, J.G. Haasnoot, J. Reedijk, Inorg. Chim. Acta 86 (1984) 137.
- [29] T.L.F. Favre, J.G. Haasnoot, J. Reedijk, Polyhedron 5 (1986) 1405.
- [30] A.T.H. Lenstra, H.J. Bruins Slot, P.T. Beurskens, J.G. Haasnoot, J. Reedijk, Recl. Trav. Chim. Pays-Bas. 108 (1989) 133.
- [31] J.M. Salas, M.A. Romero, A. Rahmani, R. Faure, Acta Crystallogr., Sect. C 50 (1994) 510.
- [32] J.G. Haasnoot, T.L.F. Favre, W. Hinrichs, J. Reedijk, Angew. Chem., Int. Ed. Engl. 27 (1988) 856.
- [33] J.M. Salas, M.A. Romero, A. Rahmani, M. Quiros, An Quim. Int. Ed. 92 (1996) 249.
- [34] J. Makisumi, H. Watanabe, K. Tori, Chem. Pharm. Bull. 12 (1964) 204.
- [35] E. Kleinpeter, R. Borsdorf, G. Fischer, H.J. Hoffmann, J. Prakt. Chem. 314 (1972) 515.
- [36] T. La Noce, A.M. Giuliani, Tetrahedron 34 (1978) 2927.
- [37] J.S. Bajwa, P.J. Sykes, J. Chem. Soc., Perkin Trans. (1979) 3085.
- [38] M. Hori, K. Tanaka, T. Kataoka, H. Shimizu, E. Jimai, K. Kimura, Y. Hashimoto, J. Chem. Soc., Perkin Trans. I (1985) 2333.
- [39] R.J. Pugmire, J.C. Smith, D.M. Grant, B. Stanovnik, M. Tisler, B. Vercek, J. Heterocycl. Chem. 24 (1987) 805.
- [40] W.W. Paudler, R.M. Sheets, B. Goodson, Org. Magn. Res. 18 (1982) 87.
- [41] M. Kuenstlinger, E. Breitmeier, Synthesis 1 (1983) 44.
- [42] L. Stefaniak, M. Witanowski, U. Mahmoud, J.D. Roberts, G.A. Webb, J. Cryst. Spectr. Res. 19 (1989) 159.
- [43] J.W. Wiench, L. Stefaniak, G.A. Webb, Magn. Res. Chem. 32 (1994) 373.
- [44] E. Kleinpeter, S. Thomas, G. Fischer, J. Mol. Struct. 355 (1995) 273.
- [45] E. Szłyk, A. Grodzicki, L. Pazderski, E. Bednarek, B. Kamieński, Polyhedron 19 (2000) 965.
- [46] P. Haake, R.M. Pfeiffer, J. Am. Chem. Soc. 92 (1970) 4996.
- [47] J. Kuduk-Jaworska, Pol. J. Chem. 59 (1985) 705.
- [48] O. Clement, A.W. Roszak, E. Buncel, Inorg. Chim. Acta 253 (1996) 53.
- [49] A. Cornia, A.C. Fabretti, M. Bonivento, L. Cattalini, Inorg. Chim. Acta 255 (1997) 405.
- [50] M. van Beusichem, N. Farrell, Inorg. Chem. 31 (1992) 634.
- [51] P.S. Pregosin, Transition Metal Nuclear Magnetic Resonance, Elsevier, Amsterdam, 1991, p. 250.

- [52] P.S. Pregosin, Coord. Chem. Rev. 44 (1982) 247.
- [53] R.K. Harris, B.E. Mann, NMR and the Periodic Table, Academic Press, London, 1978, p. 249.
- [54] P. Laszlo (Ed.) NMR of Accessible Nuclei, vol. 2, Academic Press, New York, 1983, p. 404.
- [55] G.A. Kirakosyan, Koord. Kim. (Rus.) 19 (1993) 507.
- [56] L.G. Marzilli, Y. Hayden, M.D. Reily, Inorg. Chem. 25 (1985) 974.
- [57] J.J. Pesek, W.R. Mason, J. Magn. Res. 25 (1977) 519.
- [58] S.G. de Almeïda, J.L Hubbard, N. Farrell, Inorg. Chim. Acta 193 (1992) 149.
- [59] J. Jolly, W.I. Cross, R.G. Pritchard, C.A. McAuliffe, K.B. Nolan, Inorg. Chim. Acta 315 (2001) 36.
- [60] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Chemistry, Wiley, New York, 1997, p. 24.