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Palladium(II) chloride complexes with 1,2,4-triazolo[1,5-*a*]-pyrimidines: X-ray, ^{15}N–^{1}H NMR and ^{15}N CP MAS studies

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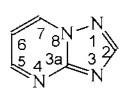
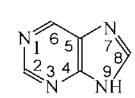
Palladium(II) complexes of formula $[Pd(tp)_2Cl_2]$ **1**, $[Pd(dmtp)_2Cl_2]\cdot H_2O$ **2**, $[Pd(dptp)_2Cl_2]\cdot H_2O$ **3**, $[Pd(dbtp)_2Cl_2]$ **4a**, **4b**, where tp = 1,2,4-triazolo[1,5-*a*]pyrimidine, dmtp = 5,7-dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidine, dptp = 5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine, dbtp = 5,7-di-*tert*-butyl-1,2,4-triazolo[1,5-*a*]pyrimidine, were prepared. The crystal structure of $[Pd(dbtp)_2Cl_2]\cdot 0.5\ C_2H_5OH$ **4c** was resolved by X-ray diffraction analysis, exhibiting monomeric, nearly square-planar *cis* geometry and N(3) co-ordination. A small tetrahedral distortion from the co-ordination plane was observed. The Pd–Cl distances are 2.276(1) and 2.283(1) Å, and Pd–N 2.042(3) and 2.040(3) Å. Spectroscopic measurements (UV-VIS, IR, NMR) suggested analogous structures for **1**, **2** and **3**. Compounds **4a** and **4b** are most likely rotational isomers in solution and distortional isomers in the solid state. ^{15}N–^{1}H heteronuclear correlation NMR was measured for **2**, **4a** and **4b** whereas **1** and **3** were characterized with ^{13}C and ^{15}N CP MAS. Significant shielding of the co-ordinated N(3) and adjacent C(2) or C(3a) nuclei was observed.

Introduction

It has been known for years that *cis*-dichloro complexes of Pt^{II} have anti-tumor properties.[1,2] However, most of them are not active against all types of cancer and have significant side effects. This is why platinum(II) chloride complexes with other N-donors, among them 1,2,4-triazolo[1,5-*a*]pyrimidine (tp) and its derivatives, are intensively studied. These heterocycles have a structure similar to that of purine and adenine, their fused ring system differing in having the pyrimidine nitrogen atom in a bridgehead position.[3–5]



1,2,4-triazolo[1,5-*a*]pyrimidine (tp)



purine

Recently anti-tumor activity of *cis*-$[Pt^{II}(Hmtpo\text{-}N^3)_2Cl_2]\cdot 2H_2O$ where HmtpO = 4,7-*H*-5-methyl-7-oxo-1,2,4-triazolo-[1,5-*a*]pyrimidine was reported.[6] Considering that also palladium(II) co-ordination compounds are promising in cancer therapy,[7] we have decided to study a class of *cis*-PdL_2Cl_2 type complexes (L = tp or its derivative). The known co-ordination compounds of Pd^{II} are mono- or poly-meric species of square-planar geometry around the central ion due to the d^8 configuration and dsp^2 hybridization.[7] This geometry was found for complexes with such heterocyclic ligands as pyridine, $[Pd(py)_2Cl_2]$, imidazole, $[Pd(Him)_2Cl_2]$, adenine, $[Pd(Had)_2Cl_2]$, $[\{Pd(Had)Cl_2\}_n]$, adenosine, $[Pd(ado)_2Cl_2]$, $[\{Pd(ado)Cl_2\}_n]$,[8–15] and 5,7-dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidine (dmtp), *trans*-$[Pd^{II}(dmtp\text{-}N^3)_2Br_2]\cdot CH_3OH$.[16] In this paper we present the crystal and molecular structure of a new co-ordination compound with a recently synthesized tp derivative, 5,7-di-*tert*-butyl-1,2,4-triazolo[1,5-*a*]pyrimidine (dbtp).[17] A series of palladium(II) chloride complexes with tp, dmtp, dbtp and 5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (dptp)[17] has been obtained and the spectral characteristics reported. The last two ligands are 5,7-disubstituted with bulky groups revealing strong π-acceptor (phenyl) or σ-donor (*tert*-butyl) properties and therefore some conformational changes in the co-ordination sphere of Pd^{II} could be expected.

Experimental

Materials

$PdCl_2$ was purchased from POCh Gliwice (Poland), tp, dmtp, 3-amino-1,2,4-triazole, 1,3-diphenylpropane-1,3-dione and 2,2,6,6-tetramethylheptane-3,5-dione of 98–99% purity from Aldrich. dptp was synthesized from 3-amino-1,2,4-triazole and 1,3-diphenylpropane-1,3-dione, dbtp from 3-amino-1,2,4-triazole and 2,2,6,6-tetramethylheptane-3,5-dione.[17]

Syntheses

The complexes were prepared in a general way as follows: 1 mmol of $PdCl_2$ was dissolved in 10 ml of a mixture of concentrated HCl and ethanol (1 : 10) and added to 2 mmol of an organic ligand diluted in 40 ml of boiling ethanol. The details of particular syntheses are given below.

***cis*-$[Pd(tp)_2Cl_2]$ 1.** The reaction mixture was heated with stirring at 75 °C, for 15 min. The precipitate was filtered off, washed with ethanol and dried in air (Found: C, 29.3; H, 1.9; N, 26.4; Pd, 25.4. $C_{10}H_8Cl_2N_8Pd$ requires C, 28.8; H, 1.9; N, 26.8; Pd, 25.5%). Yield 0.40 g (95%).

***cis*-$[Pd(dmtp)_2Cl_2]\cdot H_2O$ 2.** The reaction mixture was heated with stirring at 75 °C, for 1 hour, cooled to 5 °C and left overnight. The yellow precipitate was filtered off, washed with ethanol and dried in air (Found: C, 33.6; H, 3.5; N, 22.1; Pd, 21.4; H_2O, 3.4. $C_{14}H_{18}Cl_2N_8OPd$ requires C, 34.2; H, 3.7; N, 22.8; Pd, 21.6; H_2O, 3.7%). Yield 0.37 g (75%).

***cis*-$[Pd(dptp)_2Cl_2]\cdot H_2O$ 3.** The reaction mixture was heated with stirring at 75 °C, for 5 min. The yellow precipitate was filtered directly from hot solution, washed with boiling ethanol and dried in air (Found: C, 55.3; H, 3.5; N, 15.2; Pd, 14.0; H_2O, 2.5. $C_{34}H_{26}Cl_2N_8OPd$ requires C, 55.2; H, 3.5; N, 15.1; Pd, 14.4; H_2O, 2.4%). Yield 0.59 g (80%).

***cis*-[Pd(dbtp)$_2$Cl$_2$] 4a, 4b.** The reaction mixture was heated with stirring at 75 °C, for 15 min. The yellow precipitate (**4a**) was filtered off, washed with ethanol and dried in air. The filtrate was heated again at 75 °C for 2 h. The yellow-green precipitate (**4b**) was filtered off, washed with ethanol and dried in air (Found for **4a**: C, 48.8; H, 7.0; N, 17.1; Pd, 16.7; Found for **4b**: C, 48.5; H, 6.7; N, 17.3; Pd, 16.6. $C_{26}H_{40}Cl_2N_8Pd$ requires C, 48.6; H, 6.3; N, 17.5; Pd, 16.6%). Yield 0.27 g (42%) for **4a**, 0.24 g (37%) for **4b**.

***cis*-[Pd(dbtp)$_2$Cl$_2$]·0.5 C_2H_5OH (4c).** This compound was isolated by slow evaporation of the filtrate left after precipitation of **4a** and **4b**. Its formula and structure were determined by X-ray analysis (see below).

Measurements

^1H and ^{13}C NMR spectra were recorded with a Varian 200 XL spectrometer operating at typical frequencies. ^{15}N NMR measurements were performed with a Bruker DRX 500 spectrometer by ^{15}N–^1H heteronuclear correlation (HETCOR) techniques: for ligands by Gradient Heteronuclear Multiple-Quantum Coherence (50.66 MHz for ^{15}N, 499.80 MHz for ^1H); for complexes by Gradient Heteronuclear Single-Quantum Coherence (50.68 MHz for ^{15}N and 500.13 MHz for ^1H). The solvent was $CDCl_3$, the concentration of samples 0.05 M, the temperature 295 K, the reference standard TMS for ^1H, ^{13}C and CH_3NO_2 for ^{15}N. ^{13}C and ^{15}N CP MAS spectra were recorded with a Bruker DRX 500 spectrometer in 4 mm SB-MAS probeheads, using a standard technique (all nuclei detected) or Short Cross-Polarization Contact (protonated atoms only). The reference standard was glycine and chemical shifts were recalculated to TMS for ^{13}C {δ(CH_2 in glycine) 43.3} or to CH_3NO_2 for ^{15}N {δ(NH_2 in glycine) −347.6}. UV-VIS reflectance spectra (300–800 nm, MgO) were performed with a Specord M40 Carl Zeiss Jena spectrophotometer. IR spectra were measured with a Perkin-Elmer Spectrum 2000 FT IR spectrometer using KBr (4000–400 cm^{-1}) and polyethylene discs (400–100 cm^{-1}). Kinetic runs were studied with a Hewlett-Packard 8453 diode-array spectrophotometer, equipped with a Peltier type thermostat. C, H, N were determined by elemental semi-microanalysis, Pd gravimetrically.[18] The amount of water in the hydrated complexes **2** and **3** was calculated from thermogravimetric analysis, performed with a MOM OD-102 derivatograph (Hungary) (samples 50 mg, heating range 300–1300 K, nitrogen atmosphere, reference material α-Al_2O_3).

X-Ray crystallography

X-Ray data for compound **4c** were collected with a Kuma KM-4 diffractometer using Cu-Kα radiation, $\lambda = 1.54178$ Å at 293(2) K, by the ω–2θ method. The structure was solved by the Patterson method and refined with full-matrix least squares against F^2 using SHELX 97,[19] giving $R = 0.040$, $wR2 = 0.098$ and goodness of fit on $F^2 = 1.058$ [$I > 2\sigma(I)$]. The atomic scattering factors were taken from ref. 20. The geometry of **4c** was compared to those of other complexes using the Cambridge Structural Database.[21]

CCDC reference number 186/1819.

See http://www.rsc.org/suppdata/dt/a9/a908469j/ for crystallographic files in .cif format.

Results and discussion

The crystal structure of compound 4c

The crystal structure data of compound **4c** are listed in Table 1, selected bond lengths and angles in Table 2. The perspective view of the molecule, with its numbering scheme, is shown in Fig. 1. The asymmetric part of the unit cell contains one molecule of *cis*-[Pd(dbtp)$_2$Cl$_2$] and half of a molecule of ethanol. The triazolopyrimidine ligands are bonded to Pd^{II} *via* their N(3) atoms, the Pd(1)–N(3) distance being 2.042(3) Å and Pd(1)–N(3′) 2.040(3) Å. The chlorine atoms are in terminal positions, the Pd(1)–Cl(1) distance being 2.276(1) Å and Pd(1)–Cl(2) 2.283(1) Å. The lengths of Pd–N and Pd–Cl bonds are similar to those found in palladium(II) chloride complexes with such N-donors as pyridine, imidazole, 2,2′-bipyridine and 1,10–phenanthroline (2.011–2.063 Å for Pd–N and 2.276–2.319 Å for Pd–Cl).[21]

The N and Cl atoms in the co-ordination sphere are not exactly coplanar, their rms deviation from the Cl_2N_2 best plane being 0.014 Å. It is a result of a small tetrahedral distortion, described by the Cl(1)–N(3)–N(3′)–Cl(2) torsion angle −1.27(9)°. This type of deformation, analogous to the one observed in palladium(II) chelates,[23–25] may be caused by the steric repulsion of bulky *tert*-butyl groups in the dbtp molecules. For comparison, the central Pd^{II} is positioned in the Cl_2N_2 best plane, its deviation being only 0.002(1) Å.

The dbtp rings are planar, the rms deviations from the best planes for the N(1) to N(8) and N(1′) to N(8′) moieties being 0.012 and 0.010 Å, respectively. The Pd^{II} is displaced from these planes, its respective deviations being −0.054(4) and −0.049(4) Å for the N(1) to N(8) and N(1′) to N(8′) moieties. It indicates that the planar geometry of the co-ordinated N(3) atom (sp^2 hybridization) is slightly modified towards pyramidal. The dihedral angles between the Cl_2N_2 best plane and the ligand planes are 39.32(7) and 38.86(7)° for the N(1) to N(8) and N(1′)

Table 1 Crystallographic data for complex **4c**

Empirical formula	$C_{26}H_{40}Cl_2N_8Pd \cdot 0.5\ C_2H_6O$
M	665.02
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.7427(8)
b/Å	11.0143(5)
c/Å	14.1340(8)
α/°	75.327(4)
β/°	81.426(5)
γ/°	79.660(4)
V/Å^3	1582.10(16)
Z	2
μ/mm^{-1}	6.563
Reflections collected	6874
Reflections unique	6498
Data/parameters	6498/366
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0403, 0.0980
(all data)	0.0583, 0.1082

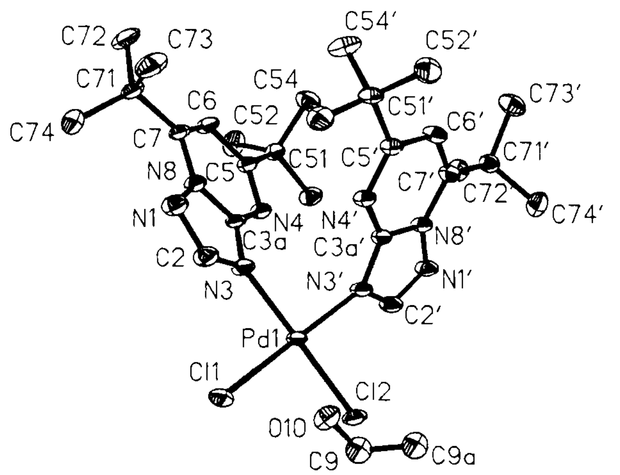


Fig. 1 The ORTEP[22] drawing of the [Pd(dbtp)$_2$Cl$_2$]·0.5 C_2H_5OH **4c** molecule.

Table 2 Selected bond lengths [Å] and angles [°] for complex **4c**

Pd(1)–N(3)	2.042(3)	Pd(1)–N(3′)	2.040(3)
Pd(1)–Cl(1)	2.276(1)	Pd(1)–Cl(2)	2.283(1)
N(8)–N(1)	1.370(4)	N(8′)–N(1′)	1.373(4)
N(1)–C(2)	1.304(5)	N(1′)–C(2′)	1.310(4)
C(2)–N(3)	1.352(4)	C(2′)–N(3′)	1.352(4)
N(3)–C(3a)	1.333(4)	N(3′)–C(3a′)	1.334(4)
C(3a)–N(8)	1.380(3)	C(3a′)–N(8′)	1.372(4)
C(3a)–N(4)	1.330(4)	C(3a′)–N(4′)	1.342(4)
N(4)–C(5)	1.322(4)	N(4′)–C(5′)	1.310(4)
C(5)–C(6)	1.427(4)	C(5′)–C(6′)	1.426(4)
C(6)–C(7)	1.357(4)	C(6′)–C(7′)	1.364(4)
C(7)–N(8)	1.384(4)	C(7′)–N(8′)	1.378(4)
Cl(1)–Pd(1)–Cl(2)	90.7(1)	N(3)–Pd(1)–N(3′)	93.3(1)
Cl(1)–Pd(1)–N(3)	87.9(1)	Cl(2)–Pd(1)–N(3′)	88.2(1)
Cl(1)–Pd(1)–N(3′)	178.5(1)	Cl(2)–Pd(1)–N(3)	178.4(1)
C(2)–N(3)–Pd(1)	125.5(2)	C(2′)–N(3′)–Pd(1)	125.2(2)
C(3a)–N(3)–Pd(1)	130.0(2)	C(3a′)–N(3′)–Pd(1)	130.9(2)
N(8)–N(1)–C(2)	102.1(3)	N(8′)–N(1′)–C(2′)	102.0(3)
N(1)–C(2)–N(3)	115.9(3)	N(1′)–C(2′)–N(3′)	116.0(3)
C(2)–N(3)–C(3a)	104.3(3)	C(2′)–N(3′)–C(3a′)	103.9(3)
N(3)–C(3a)–N(8)	107.4(3)	N(3′)–C(3a′)–N(8′)	108.1(3)
C(3a)–N(8)–N(1)	110.2(3)	C(3a′)–N(8′)–N(1′)	110.0(3)
C(3a)–N(4)–C(5)	116.5(3)	C(3a′)–N(4′)–C(5′)	116.4(3)
N(4)–C(5)–C(6)	121.5(3)	N(4′)–C(5′)–C(6′)	122.0(3)
C(5)–C(6)–C(7)	122.5(3)	C(5′)–C(6′)–C(7′)	122.1(3)
C(6)–C(7)–N(8)	114.1(3)	C(6′)–C(7′)–N(8′)	113.8(3)
C(7)–N(8)–C(3a)	121.6(3)	C(7′)–N(8′)–C(3a′)	122.3(3)
N(8)–C(3a)–N(4)	123.9(3)	N(8′)–C(3a′)–N(4′)	123.3(3)

to N(8′) moieties, respectively. The dihedral angle between the ring systems of both triazolopyrimidine ligands is 51.56(8)°.

The displacement of ternary carbons of the *tert*-butyl groups from the ligand best planes is more pronounced for C(51) or C(51′) (−0.111(3) and 0.121(5) Å, respectively) than for C(71) or C(71′) (0.030(6) and −0.046(5) Å respectively). It is also interesting that the C–C bond distances and C–C–C angles inside these substituents are in a relatively broad range, varying from 1.512(4) to 1.540(5) Å and from 107.5(3) to 111.4(3)°, respectively. These observations confirm the occurrence of steric effects associated with the presence of *tert*-butyl groups.

The ethanol molecule lies outside the co-ordination sphere and is positioned near the center of symmetry [1/2,0,0] that relates its two carbon atoms. Such positioning results in disorder. The only polar intermolecular interactions found in the crystal packing are those formed by the ethanol O(10)H group (site occupancy factor of 50%) with the Cl(2) [*x*,*y*,*z*] ions, the respective distances being 2.519 Å for the H · · · Cl(2) bonding and 3.277 Å for the O(10) · · · Cl(2). The O–H · · · Cl(2) angle is 154.2°.

NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra of tp and dmtp were reported by many authors.[26–31] The ^{15}N NMR spectrum of tp was also published but the assignment of resonances was the subject of literature controversies.[32–36] Recently we have assigned those signals using the ^{15}N–^{1}H HETCOR method.[37] Selective decoupling techniques for ^{1}H, ^{13}C and ^{15}N NMR measurements of dmtp, dptp and dbtp were also applied.[17] During this work we have measured ^{15}N–^{1}H HETCOR spectra for all discussed tp derivatives, assigning ^{15}N resonances (for dmtp, Fig. 2) as previously:[17] N(1) and N(3) are coupled with H(2), N(4) with the CH_3 group at C(5) and N(8) with H(2), H(6) and the CH_3 group at C(7). The N(1) and N(3) signals can be identified on the basis of their chemical shifts. It has been demonstrated by many authors that in triazolopyrimidine ring systems the N(3) nucleus is much more shielded than the other pyridine-type nitrogens, *i.e.* N(1) and N(4).[32–36]

The discussed palladium(II) complexes decompose in d_6-dmso, therefore we have performed NMR measurements in $CDCl_3$ (**2**, **4a**–**4c**) or in the solid phase (**1**, **3**), the data being collected in Tables 3–5. For comparison, we have measured also the ^{13}C and ^{15}N CP MAS spectra for the ligands tp and dptp (Tables 4, 5).

Table 3 ^{1}H NMR chemical shifts (δ) of dmtp, dbtp and their palladium(II) chloride complexes, in $CDCl_3$ (co-ordination shifts in parentheses)

Compound	H(2)	H(6)	R[a]
dmtp	8.37	6.79	2.62; 2.75
2	8.71 (+0.34)	6.98 (+0.19)	2.77; 2.83
dbtp	8.43	7.00	1.44; 1.61
4a	9.04 (+0.61)	6.87 (−0.13)	0.94; 1.52
4b	8.65 (+0.22)	7.11 (+0.11)	1.53; 1.57

[a] R = CH_3 for dmtp, $C(CH_3)_3$ for dbtp.

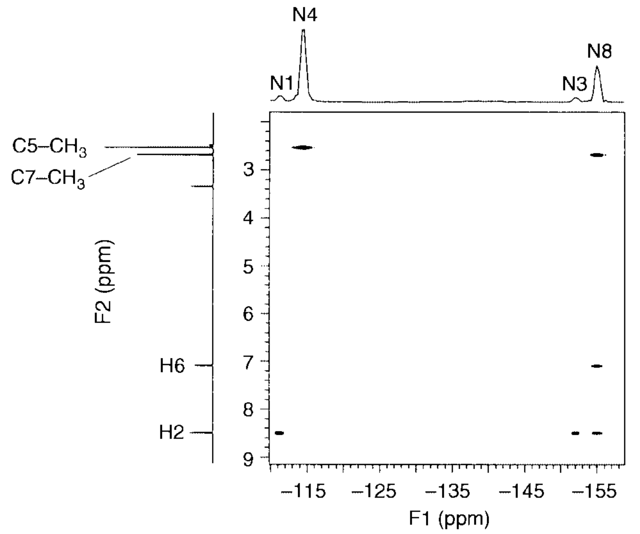


Fig. 2 HETCOR ^{15}N–^{1}H NMR spectrum of dmtp.

The co-ordination of triazolopyrimidine molecules by Pd^{II} results in the shift of ^{1}H and ^{13}C signals (Tables 3, 4). The ^{1}H resonances have been shifted in both directions of the frequency scale (maximum 0.6 ppm). For ^{13}C NMR a clear pattern of the co-ordination shifts has been observed for the complexes of dmtp and dbtp (**2**, **4a**–**4c**), for which the measurements were performed in $CDCl_3$. The C(2) and C(3a) signals have been shifted upfield (maximum 3.6 ppm), C(5), C(6) and C(7) downfield (maximum 3.6 ppm). This fact indicates that these two ligands co-ordinate *via* N(3). Analogous results were found for palladium(II) and platinum(II) chloride complexes with pyrimidine derivatives.[38–42] For the complexes of tp and dptp (**1**, **3**), the results of ^{13}C NMR measurements in the solid phase are not so apparent and do not allow one unambiguously to determine the metallation sites. The shifts of signals are large (maximum 6.8 ppm) but there is no correlation between their direction or magnitude and the position of a carbon atom in the heterocyclic ring. Most likely, the local magnetic fields are strongly influenced by the orientation or packing of the molecules in the crystal lattice.

In the ^{15}N NMR spectra of the examined complexes a large upfield shift (78–90 ppm) of one of the resonances was observed (Table 5). For **2**, **4a** and **4b** this signal was unambiguously assigned to N(3) by ^{15}N–^{1}H HETCOR measurements. In the case of **1** and **3**, for which the CP MAS spectra were recorded and compared to those of tp and dptp, it could be related to N(3) or N(8). However, the latter possibility can be excluded, because N(8) is a pyrrole-type nitrogen which is unable to co-ordinate with Pd^{II} and co-ordination occurs *via* N(3).

The observed upfield shift of the N(3) signal is comparable to the one resulting upon protonation of this nitrogen atom in tp

Table 4 ^{13}C NMR chemical shifts (δ) of 1,2,4-triazolo[1,5-*a*]pyrimidines and their palladium(II) chloride complexes, in $CDCl_3$ or solid phase (co-ordination shifts in parentheses)

Compound	C(2)	C(3a)	C(5)	C(6)	C(7)	R[a]
tp$^{solid\ b}$	154.7	154.1	156.7	109.9	138.7	—
1^{solid}	159.0 (+4.3)	151.1 (−3.0)	159.0 (+2.3)	116.7 (+6.8)	138.8 (+0.1)	—
dmtp^{CDCl_3}	155.1	155.0	164.6	110.5	146.5	16.8; 24.8
2^{CDCl_3}	154.0 (−1.1)	152.1 (−2.9)	168.2 (+3.6)	112.9 (+2.4)	147.9 (+1.4)	16.5; 25.4
dptp^{solid}	158.0	156.4	161.4	105.8	149.1	125–140
3^{solid}	153.5 (−4.5)	152.8 (−3.6)	161.2 (−0.2)	105.2 (−0.6)	147.0 (−2.1)	125–140
dbtp^{CDCl_3}	154.3	156.0	175.6	103.2	157.4	36.1; 38.6; 26.9; 29.5
4a^{CDCl_3}	154.3 (0.0)	152.4 (−3.6)	177.6 (+2.0)	104.4 (+1.2)	158.9 (+1.5)	36.4; 38.5; 26.9; 29.0
4b^{CDCl_3}	153.0 (−1.3)	152.7 (−3.3)	178.3 (+2.7)	105.2 (+2.0)	158.3 (+0.9)	36.2; 39.3; 26.9; 29.5

[a] R = H for tp, CH_3 for dmtp, C_6H_5 for dptp, $C(CH_3)_3$ for dbtp. [b] Data from our earlier paper.[37]

Table 5 ^{15}N NMR chemical shifts (δ) of 1,2,4-triazolo[1,5-*a*]pyrimidines and their palladium(II) chloride complexes, in $CDCl_3$ or solid phase (co-ordination shifts in parentheses)

Compound	N(1)	N(3)	N(4)	N(8)
tp$^{solid\ a}$	−107.2	−154.7	−107.2	−154.7
1^{solid}	−106.0 (+1.2)	−242.5 (−87.8)	−103.7 (+3.5)	−155.4 (−0.7)
dmtp^{CDCl_3}	−109.7	−151.0	−111.7	−152.8
2^{CDCl_3}	−109.8 (−0.1)	−240.2 (−89.2)	−114.2 (−2.5)	−157.2 (−4.4)
dptp^{solid}	−108.3	−151.2	−120.7	−155.7
3^{solid}	−109.5 (−1.2)	−239.1 (−87.9)	−125.0 (−4.3)	−163.8 (−8.1)
dbtp^{CDCl_3}	−106.4	−155.1	−114.2	−157.5
4a^{CDCl_3}	−107.4 (−1.0)	−233.3 (−78.2)	−120.1 (−5.9)	−162.1 (−4.6)
4b^{CDCl_3}	−106.3 (+0.1)	−242.6 (−87.5)	−113.9 (+0.3)	−161.4 (−3.9)

[a] N(1)/N(4) and N(3)/N(8) signals in the CPMAS spectrum of tp are not separated.[37]

(78 ppm).[35] This complexation shift is much more significant than observed for zinc(II) or gold(III) triazolopyrimidine chloride complexes (1–2 and 8–10 ppm respectively),[37,43,44] but smaller than for analogous platinum(II) compounds (92–96 ppm).[44] Similar co-ordination shifts of ^{15}N resonances were already described for a series of palladium(II) aqua- and chloro-complexes with ammonia (35–55 ppm).[45]

The shielding of atom N(3) (as well as of adjacent carbons C(2) and C(3a)) is most likely caused by involvement of its lone-pair electrons in the co-ordination bonding. This process is accompanied by a slight modification of the trigonal geometry of N(3) towards pyramidal (see **4c** structure discussion), which suggests that this nitrogen partially changes its sp^2 hybridization and becomes closer to sp^3. The lone-pair electrons impact on the value of the shielding tensor can be illustrated by the comparison of pyridine-type nitrogens in azines with much more shielded pyrrole-type atoms in azoles.[46] The phenomenon of the upfield shift of ^{15}N resonances (50–150 ppm) was observed for many heteroaromatic ring systems upon protonation, N-oxidation or platinum(II) complexation.[47,48] The nitrogen co-ordination shift is sensitive to the presence of a lone pair on nitrogen and π-electron delocalization. In transition metal complexes d-electron pair shift onto nitrogen is also possible resulting in nitrogen shielding.[49,50] The upfield co-ordination shift of π-bonded nitrogen can be related to the removal of the low energy $n(N) \longrightarrow \pi^*$ circulation and stabilization by binding to the metal ion.

Table 6 Selected IR bands/cm^{-1} for 1,2,4-triazolo[1,5-*a*]pyrimidines and their palladium(II) chloride complexes (co-ordination shifts in parentheses)

Compound	ν_{tp}	ν_{py}
tp	1621	1534; 1515
1	1616 (−5)	1538; 1519 (+4; +4)
dmtp	1637	1550
2	1640 (+3)	1552 (+2)
dptp	1612	1543
3	1615 (+3)	1553 (+10)
dbtp	1615	1530
4a	1617 (+2)	1537 (+7); 1547 (+17)
4b	1618 (+3)	1536 (+6); 1547 (+17)
4c	1616 (+1)	1538 (+8); 1547 (+17)

Table 7 Far-IR bands/cm^{-1} for palladium(II) chloride complexes with 1,2,4-triazolo[1,5-*a*]pyrimidines

Compound	ν(Pd–Cl)	ν(Pd–N)
1	360, 306	285, 245
2	356, 338	296, 280
3	352, 325	286, 272
4a	364, 341	324, 300
4b	356, 336	307, 297
4c	363, 341	324, 299

Infrared spectroscopy

The two most characteristic bands in the IR spectra of tp and its derivatives, ν_{tp} (1612–1637 cm^{-1}) and ν_{py} (1515–1550 cm^{-1}), were assigned to an overall triazolopyrimidine and the pyrimidine ring mode vibrations.[37] The co-ordination by Pd^{II} results in a shift of these bands towards higher frequencies (maximum 18 cm^{-1}). This effect, similar to the one observed for analogous zinc(II) complexes,[37,43] is more profound for ν_{py} than for ν_{tp} (Table 6).

In the range 100–400 cm^{-1} four new absorption bands, not present in the ligands spectra, have been detected (Table 7). Two, found in the range 306–364 cm^{-1}, can be assigned to Pd–Cl stretching vibrations as they are similar to those found for palladium(II) salts and co-ordination compounds such as $PdCl_2$ (343 cm^{-1}), $PdCl_4^{2-}$ (321 cm^{-1}), *trans*-$[PdCl_2(NH_3)_2]$ (333 cm^{-1}), *cis*-$[PdCl_2(NH_3)_2]$ (306, 327 cm^{-1}), *trans*-$[Pd(py)_2Cl_2]$ (358 cm^{-1}), *cis*-$[Pd(py)_2Cl_2]$ (333, 342 cm^{-1}), *trans*-$[Pd(Him)_2Cl_2]$ (373 cm^{-1}) and *cis*-$[Pd(Him)_2Cl_2]$ (335, 339 cm^{-1}).[8–10,51,52] The two bands, found in the range 245–324 cm^{-1}, can be allocated to Pd–N stretching modes, as was reported for *trans*-$[Pd(py)_2Cl_2]$ (278 cm^{-1}) and *cis*-$[Pd(py)_2Cl_2]$ (266, 276 cm^{-1}).[8,9]

Assuming the square-planar configuration around Pd^{II}, one can expect from group theory calculations one Pd–Cl and one Pd–N stretching vibration (IR-active) for *trans* isomers (symmetry D_{2h}) or two of each mode for *cis* forms (C_{2v}).[51] Therefore, the presence of four bands in the far-IR spectra of all studied complexes is in favor of their C_{2v} symmetry.

In the IR spectra of complexes **2** and **3** one can observe broad absorption bands in the range 3450–3550 cm^{-1}, deriving from O–H stretching vibrations of the water molecules. Their energy is about 200 cm^{-1} smaller than for free water (3755 and 3655 cm^{-1})[53,54] and typical for lattice water.[51] The deformation vibrations of H–O–H, expected in the 1600–1650 cm^{-1} range, cannot be observed as they are overlapped by intense ν_{tp} bands of the triazolopyrimidine ligands. The molecules of H_2O are most likely hydrogen bonded to chlorine atoms, as for ethanol in **4c** or for lattice water in a ruthenium(III) complex, $[Ru(dmtp)_2Cl_3(H_2O)]\cdot H_2O$.[55] However, they can also occupy the axial positions in the co-ordination sphere of the central ion, which is common in the chemistry of Pd and Pt.[56] A similar mode of binding of solvent molecules, by van der Waals forces, was described for methanol in *trans*-$[Pd^{II}(dmtp\text{-}N^3)_2Br_2]\cdot CH_3OH$.[16]

Electronic spectroscopy

In the UV-VIS spectra of complexes **1** and **2** the absorption bands have been observed at 340–350, 410–420 and 500–510 nm. Assuming C_{2v} symmetry around Pd^{II} one can suggest that they derive from the spin allowed d–d transitions: $^1A_{1g} \longrightarrow {}^1A_{2g}$, $^1A_{1g} \longrightarrow {}^1E_g$, $^1A_{1g} \longrightarrow {}^1B_{1g}$, from the $d_{xy}(b_{2g})$, $d_{xz,yz}(e_g)$ and $d_{z^2}(a_{1g})$ orbitals to the empty $d_{x^2-y^2}$ level.[57] In the spectrum of **3** only two shoulders are observed at 340 and 375 nm, due to overlapping by intense LMCT transitions.

Complexes **4a** and **4b** significantly differ in their electronic spectra. The former reveals an absorption band at 388 nm, the latter at 345 and 417 nm. In freshly prepared chloroform solutions the shape of the absorption curves for the two compounds is similar to the one in the solid state, the respective maxima being observed at 382 nm for **4a**, 338 and 407 nm for **4b**.

Studies of tautomerism between complexes 4a and 4b

Complexes **4a** and **4b** have an identical stoichiometric formula, similar *cis* geometry and the same N(3) co-ordination site but they reveal different spectroscopic properties (NMR, UV-VIS, far-IR). Their detailed geometry is not known, however the spectral characteristic of **4a** is virtually the same as that of **4c**. This indicates that **4a** has a structure nearly identical to that of **4c**, although the stoichiometry of these two compounds is different. In the solid state **4a** and **4b** are stable and no tautomerism is observed at 0–150 °C. However, when dissolved in chloroform or acetone, they isomerize to a mixture containing both forms of $[Pd(dbtp)_2Cl_2]$. Integration of ^1H NMR signals (295 K) demonstrates that in $CDCl_3$ there is 26% of **4a** and 74% of **4b** ($K_{AB} = 2.85$), in d_6-acetone 84% of **4a** and 16% of **4b** ($K_{AB} = 0.19$). In the latter solvent the ^1H chemical shifts of H(2) and H(6) were δ 9.03 and 7.24 for **4a**, δ 8.75 and 7.47 for **4b**.

^1H NMR variable temperature experiments revealed that in $CDCl_3$ the ratio **4a** : **4b** was strongly dependent on temperature, varying from 1 : 4 at 303 K to 7 : 4 at 328 K. This suggests that both complexes are rotational isomers, formed by the restrained rotation of the dbtp ligands about the Pd–N(3) or Pd–N(3′) bond. The distinct orientation of the triazolopyrimidine rings results in the observed differences in the NMR spectra of both complexes. This phenomenon is probably affected by the steric hindrance of the bulky *tert*-butyl groups of the dbtp molecules.

The described distortions (see structure discussion) from square-planar geometry of the central ion in complex **4c** are similar to those reported for a few palladium(II) complexes with derivatives of 2,2′-bipyridine and 1,10-phenanthroline.[58,59] For those compounds the deformations were associated with the coexistence of distortional isomers in the crystal lattice. This kind of isomerism is defined as involving two or more equilibrium arrangements of ligands, differing in the structural nuances of the co-ordination polyhedron.[60–62] In our opinion, obtained as pure species, **4a** and **4b** can be regarded either as rotational isomers in solution or distortional ones in the solid state.

The kinetics of the isomerization reaction (1) for both forms

$$\mathbf{4a} \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} \mathbf{4b} \qquad K_{AB} = k_{ab}/k_{ba} \tag{1}$$

of $[Pd(dbtp)_2Cl_2]$ has been studied by electronic spectroscopy. The absorption curves (320–550 nm) of pure complexes **4a** and **4b** as well as of their equilibrium mixture are presented in Fig. 3 ($CHCl_3$, 25 °C, 0.002 M Pd^{II}). The kinetic runs, carried out under the above mentioned conditions, and the typical changes with the reaction course are presented at Fig. 4. The existence of three isosbestic points (at 333, 359 and 410 nm) confirms the proposed reaction stoichiometry. The runs were performed starting from either **4a** or **4b** and gave the same observed rate constants, calculated for the range 320–550 nm with a SPECFIT program:[63] $k_{obs} = (k_{ab} + k_{ba}) = 2.5 \times 10^{-4} \pm 3 \times 10^{-5}$ s^{-1}; $k_{ab} = 1.9 \times 10^{-4}$ s^{-1}; $k_{ba} = 0.6 \times 10^{-4}$ s^{-1}. The value of equilibrium constant $K_{AB} = k_{ab}/k_{ba} = 3.2$ which differs less than 10% from the one determined by ^1H NMR.

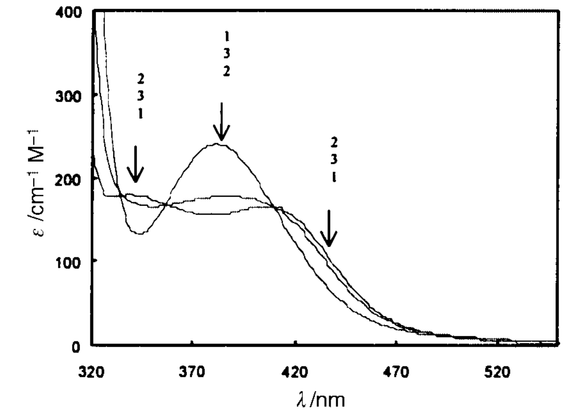


Fig. 3 The electronic spectra of isomers **4a** (1), **4b** (2) and their equilibrium mixture (3); $CHCl_3$, 25 °C, $[Pd^{II}]_T = 0.002$ M.

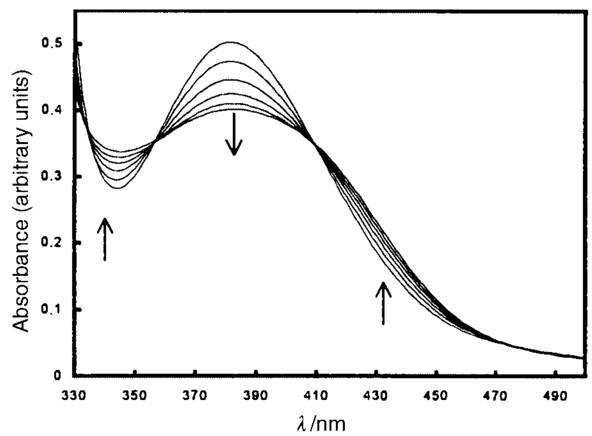


Fig. 4 Spectral changes observed during the isomerization reaction **4a** ⟶ **4b**; $CHCl_3$, 25 °C, $[Pd^{II}]_T = 0.002$ M.

Conclusion

The present study describes a series of *cis*-dichloro complexes of Pd^{II} with tp and its 5,7 derivatives. The observed co-ordination mode *via* N(3) may be regarded as representative for these heterocycles and analogous to N(9) complexation in purines. The crystal structure of **4c** is the first one reported for the novel dbtp ligand and exhibits tetrahedral distortion from the square-planar geometry. Such unusual deformation can be related to the steric strains caused by bulky *tert*-butyl substituents. The two other dbtp complexes, **4a** and **4b**, undergoing tautomeric reactions in non-co-ordinating solvents, can probably be regarded as rotational isomers in the solutions and distortional ones in the solid phase.

The palladium(II) complexation results in a large upfield shift of ^{15}N NMR signals of co-ordinated nitrogens (*ca*. 80–90 ppm) and adjacent carbons (maximum 3.6 ppm). The magnitude of the observed shielding is much higher than for analogous zinc(II) and gold(III) complexes but lower than for platinum(II) ones.

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