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TWO UNEXPECTED STRUCTURES OF PLATINUM GROUP METAL COMPLEXES WITH 1,2-DIHYDRO-2,5-DIPHENYL-3H-1,2,4-TRIAZOLE-3-THON

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ABSTRACT

Palladium (II) and platinum (II) complexes 5 and 6 were synthesized using 1,2-dihydro-2,5-diphenyl-3H-1,2,4-triazole-3-thion 3 as a ligand from an isomeric mixture of 3 and 4. The unexpected structures of 5 and 6 were investigated by mass spectra, IR (DRIFT), and ESCA measurements as well as crystal structure determinations. The palladium (II) complex is tetranuclear with two groups of Pd central atoms with different coordination geometries. Two Pd atoms have coordination number 5 (square pyramidal) with a weak Pd-Pd bond between both coordination centers. The other Pd atoms show coordination number 4 (square planar). In the structure of the platinum (II) complex anion the Pt atom is surrounded by four sulphur atoms of the thion groups arranged in a square planar coordination. The crystal structure shows an extended system of hydrogen bonds that obviously determine the configuration of the complex anion.

Key words: Palladium and platinum (II) complexes; structures; triazole-3-thion; square planar and square pyramidal coordination; Pd-Pd coordination; anionic platinum complex.

DOS ESTRUCTURAS INESPERADAS DE COMPLEJOS METÁLICOS DEL GRUPO DEL PLATINO CON 1,2-DIHDRO-2,5-DIFENIL-3H-1,2,4-TRIAZOL-TIONA

RESUMEN

Los complejos de paladio (II) 5 y platino (II) 6 fueron sintetizados utilizando como ligando el 1,2-dihidro-2,5-difenil-3H-1,2,4-triazol-3-tiona 3 a partir de una mezcla de los isómeros 3 y 4. Las inesperadas estructuras de 5 y 6 fueron investigadas por el espectro de masas, IR (DRIFT) y por mediciones ESCA; así como por determinación de las estructuras cristalinas. El complejo de paladio (II) es tetranuclear, con dos grupos de átomos centrales de paladio de diferente geometría de coordinación. Dos átomos de paladio tienen coordinación 5 (pirámide cuadrada) con un enlace débil Pd-Pd entre ambos centros de coordinación. Los otros átomos de paladio presentan número de coordinación 4 (cuadrada plana).

En la estructura del anión complejo de platino (II), el átomo de Pt está rodeado por cuatro átomos de azufre del grupo tiona, en un arreglo de coordinación cuadrada plana. La estructura cristalina presenta un sistema amplio de enlaces de hidrógeno que obviamente determinan la configuración del anión complejo.

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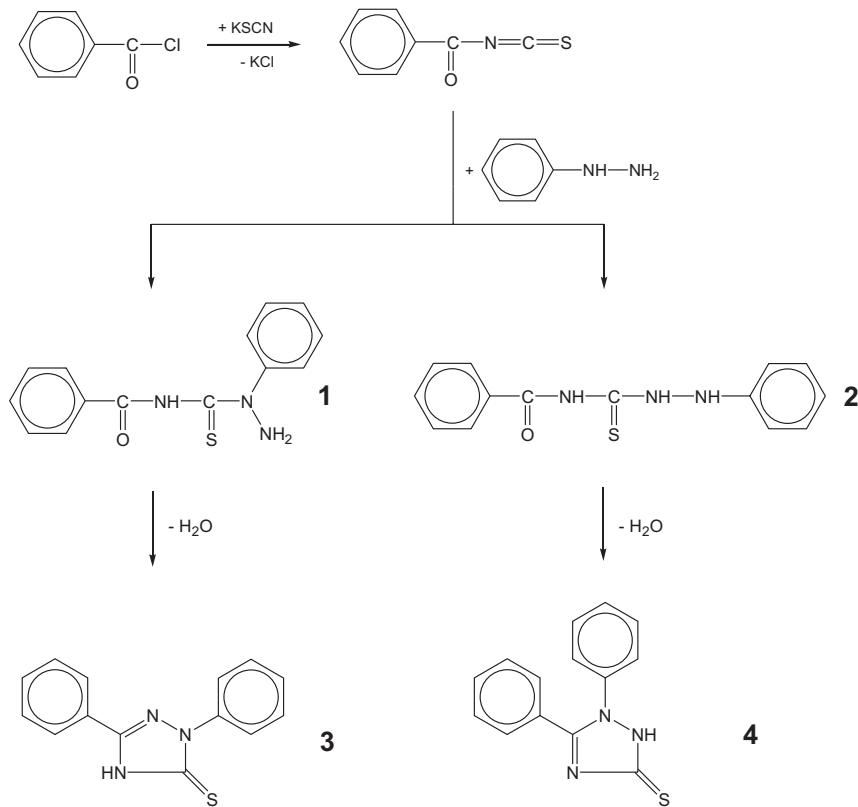
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Palabras clave: Complejos de paladio(II) y platino(II); estructura; triazol-3-tiona; coordinación cuadrada plana y piramidal cuadrada; coordinación Pd-Pd; complejo aniónico de platino.

INTRODUCTION

Acyl isothiocyanates which are easily obtained from acyl chlorides and potassium thiocyanate react with primary or secondary amines to N'-monosubstituted or N,N'-disubstituted N-acyl thioureas. These classes of substances have been thoroughly investigated since long time because of their ability for complex formation and their interesting extraction properties^{1,2}.

By reaction of acyl isothiocyanates with hydrazine or substituted hydrazines N-acyl thiourea derivatives should be formed as intermediates in same manner. In case of phenyl hydrazine the reaction can take place with both the NHC_6H_5 group and the NH_2 group (scheme 1).



Scheme 1

Therefore, two different reaction products are imaginable by use of benzoyl isothiocyanate: N'-amino-N'-phenyl-N-benzoyl thiourea 1 and N'-anilino-N-benzoyl thiourea 2.

However, both products react by dehydration and cyclization with formation of isomeric triazoles:

1,2-dihydro-2,5-diphenyl-3H-1,2,4-triazole-3-thion 3 und 1,2-dihydro-1,5-diphenyl-3H-1,2,4-triazole-3-thion 4.

Whereas the compounds 3 and 4 have already been synthesized by different ways and characterized in detail (3³⁻⁷, 4³⁻⁸), the synthesis described by Angulo et al.⁹ gives a mixture of both isomers.

In this paper the structures of a palladium(II) complex 5 and a platinum(II) complex 6 are reported which are formed from the isomeric mixture of 3 and 4 with the isomer 3.

EXPERIMENTAL

All chemicals and solvents were dried and purified by the usual methods.

Mass spectra

High resolution mass spectra (ESI positiv) were measured with a FT ICR MS APEX II (Bruker Daltonics) spectrometer and methanol as a solvent.

IR (DRIFT)

The DRIFT spectrum of the platinum metal complex 6 was measured in the middle infrared region (4000 – 400 cm⁻¹) with a System 2000R spectrometer (Perkin-Elmer) by using a Praying Mantis diffuse reflection attachment (Harrick). The spectrum was recorded at a resolution of 4 cm⁻¹, with 32 scans being averaged. KBr was used as a standard (background).

ESCA

The ESCA spectra were recorded with a VG ESCALab 220iXL photoelectron spectrometer using unmonochromatised Al K α radiation (12 kV, 20 mA). The powder samples were spread on double-side adhesive carbon tape fixed on stainless steel sample holders. Charging effects were compensated setting the C 1s value of the carbon contamination to 285,0 eV. During the measurements the vacuum was in the low 10⁻⁸ Torr region.

Crystal structure determinations

The data for the crystal structure determinations were collected with a Siemens-SMART diffractometer (5) and a Stoe-IPDS-2T diffractometer (6) using MoK α radiation ($\lambda=0.71073$ Å) at measuring temperatures of 220 K (5) and 170 K (6). Absorption corrections were performed for the Pd complex 5 with SADABS and for the Pt complex 6 with X-RED and X-SHAPE. The structures were solved by direct methods and refined anisotropically¹⁰. The H atom positions in 5 were calculated geometrically with fixation of the U_{iso} values. In 6 the H atoms in the water molecules and in the triethylammonium ions were estimated experimentally and refined isotropically. All other H atoms were calculated geometrically with fixation of the U_{iso} values.

Details of crystal data and structure determinations are summarized in table 5.

Further details of the crystal structure determinations are available on request from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the deposition numbers CCDC-713057 (5) and CCDC-713058 (6), the name of the authors, and the journal citation.

Synthesis of 5

2,1 mmol (89 mg) LiCl are dissolved in 15 mL freshly distilled methanol. To this solution 1,0 mmol (177 mg) PdCl₂, dissolved in 30 mL methanol, is added. The dark red solution is refluxed for 4 h at 60°C with permanent stirring. The complex Li₂PdCl₄ is formed. To this solution a solution of 2,1 mmol (532 mg) of the isomeric mixture 1,2-dihydro-2,5-diphenyl-

*3H-1,2,4-triazole-3-thion/1,2-dihydro-1,5-diphenyl-3*H*-1,2,4-triazole-3-thion*⁹, dissolved in 15 mL methanol, is added. The reaction mixture is refluxed for 10 h at 70°C with permanent stirring. The colour first changes to brick-red and later to dark red.

After finishing the reaction the solution is stored for 24 h. After that the reaction product is isolated by filtration and washed with cold methanol. The dark red solid is recrystallized by DMF. $C_{84}H_{60}Cl_2N_{18}Pd_4S_6$, M 2010.36 g/mol. Yield 40%. Found (calc.) C 53,2 (50,2), N 10,3 (12,5), S 8,37 (9,57), Cl 2,87 (3,53) %.

Synthesis of 6

0,12 mmol (50 mg) K_2PtCl_4 are dissolved in 25 mL methanol and 1 mL water. To this solution 0,48 mmol (122 mg) of the isomeric mixture 1,2-dihydro-2,5-diphenyl-3*H*-1,2,4-triazole-3-thion/1,2-dihydro-1,5-diphenyl-3*H*-1,2,4-triazole-3-thion⁹, dissolved in ethanol, is added, together with 1 mL triethylamine. The solution is vigorously stirred for 3 h under slight heating and accepts a light yellow colour. After finishing the reaction the solution is stored overnight. Then the main part of the solvent is removed and the solution is stored in the refrigerator. The formed precipitate is filtered and dissolved in a mixture of chloroform and hexane (1:2). From this solution red-orange crystals precipitate in the refrigerator. $[(C_2H_5)_3NH_2][Pt(C_{14}H_{10}N_3S)_4]$, M 1408,75 g/mol. Yield 83 mg (48,91%). Found (calc.) C 57,50 (57,98), H 5,32 (5,15), N 13,53 (13,92), S 8,89 (9,10) %.

RESULTS AND DISCUSSION

Structure of 5

1,2-Dihydro-2,5-diphenyl-3*H*-1,2,4-triazole-3-thion 3 forms with lithium tetrachloropalladat(II) a tetranuclear Pd complex (fig. 1). This complex contains two groups of Pd central atoms, which are different in their coordination geometry.

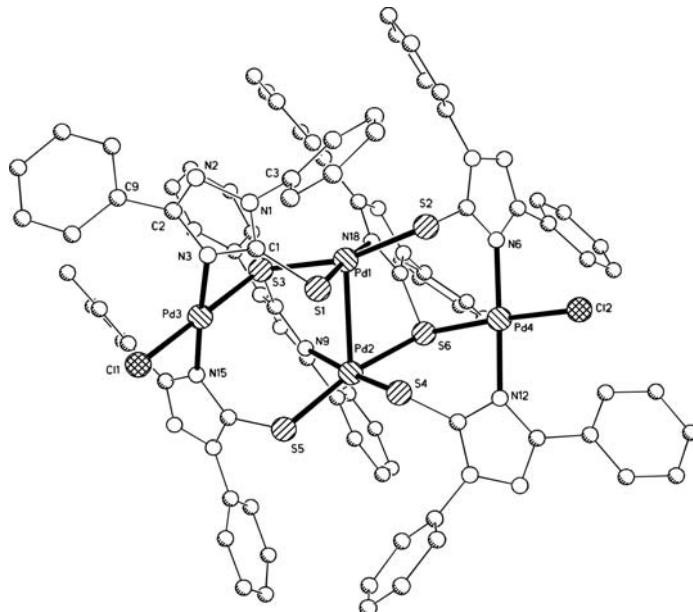


Figure 1. Molecular structure of Pd complex 5 (without hydrogen atoms)

The coordination geometry of Pd1 and Pd2 is square pyramidal. The square basic planes are occupied by three sulphur and one nitrogen ligator atoms, the tops by the respective other Pd atom (coordination number 5). Pd3 and Pd4 are coordinated square planar by one sulphur, two nitrogen and one chlorine ligator atoms (coordination number 4).

Only S1, S2, S4 and S5 coordinate of the six sulphur atoms with one Pd atom, while S3 and S6 are bridging ligators between two Pd atoms. All six ligand molecules coordinate by deprotonation with S and N to two Pd central atoms.

Selected bond lengths are given in table 1. The distance Pd1-Pd2 is 3,031 Å and shows a weak intramolecular Pd-Pd bond^[11]. The bond lengths in the planar triazole rings of the coordinated ligands are compatible with those in 1,2,4-triazole^[12,13] and reflect the contribution of several resonance structures to the ground state of the heterocycle. The shortest N-C bond is the formal double bond N2-C2 (mean value of all six triazole rings 1,321 Å). It is followed by the formal single bonds N3-C1 (1,342 Å), N1-C1 (1,350 Å) and N3-C2 (1,373 Å). There are no hydrogen bonds in the crystal structure.

Table 1. Selected bond lengths (Å) in 5

Pd1 – Pd2	3,031(1)		
Pd1 – S1	2,318(1)	Pd2 – S4	2,285(1)
Pd1 – S2	2,321(1)	Pd2 – S5	2,338(1)
Pd1 – S3	2,358(1)	Pd2 – S6	2,385(1)
Pd1 – N18	2,046(3)	Pd2 – N9	2,068(3)
Pd3 – S3	2,277(1)	Pd4 – S6	2,327(1)
Pd3 – Cl1	2,313(1)	Pd4 – Cl2	2,295(1)
Pd3 – N3	2,028(3)	Pd4 – N6	2,039(3)
Pd3 – N15	2,014(3)	Pd4 – N12	2,034(3)

Mean values of the six triazole rings

S1 – C1	1,732(3) and 1,756(3) (bridging)		
N1 – N2	1,368(4)	N1 – C1	1,350(4)
N1 – C3	1,438(4)	N2 – C2	1,321(4)
N3 – C1	1,342(4)	N3 – C2	1,373(4)
C2 – C9	1,476(5)		

Structure of 6

1,2-Dihydro-2,5-diphenyl-3H-1,2,4-triazole-3-thion 3 forms with potassium tetrachloroplatinat(II) and triethylamine a complex of the composition $[(C_2H_5)_3NH]_2[Pt(C_{14}H_{10}N_3S)_4]$ whose crystal structure contains two molecules water and three molecules chloroform per formula unit (fig. 2).

In the complex anion four ligands coordinate under deprotonation by the sulphur atoms of the thion groups that surround the Pt atom in a nearly square planar arrangement.

Selected bond lengths are given in table 2. Here the bond lengths in the planar triazole rings of the coordinated ligands are also compatible with those in 1,2,4-triazole. The shortest N-C bond is again the formal double bond N2-C2 (mean value of all four triazole rings 1,324 Å). As well as in 5 the formal single bonds N3-C1 (1,339 Å), N3-C2 (1,365 Å) and N1-C1 (1,367 Å) are clearly longer.

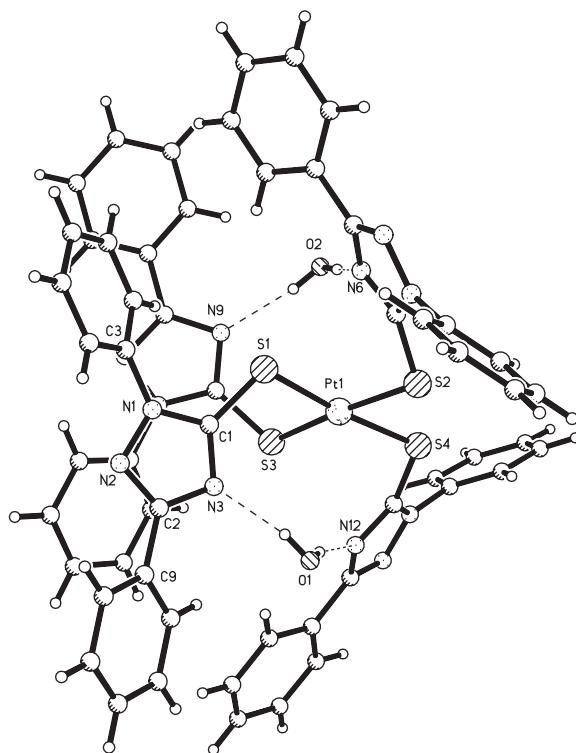


Figure 2. Molecular structure of the complex anion of Pt complex 6

Table 2. Selected bond lengths (Å) in 6

S1 – C1	1,734(3)	N1 – N2	1,374(3)
N1 – C1	1,367(4)	N1 – C3	1,427(4)
N2 – C2	1,324(4)	N3 – C1	1,339(4)
N3 – C2	1,365(4)	C2 – C9	1,472(4)

The crystal structure shows an interesting system of hydrogen bonds that obviously determine the configuration of the complex anion. In each case two triazole rings are connected by a water molecule as H donor (bridges to N3/N12 and N6/N9). Simultaneously, both water molecules are also H acceptors for the H atoms of the triethylammonium cations (table 3). Additionally, the crystal structure contains three chloroform molecules per complex anion that show no interactions with other parts of the structure. The structural parameters of the triethylammonium ions and the chloroform molecules are in agreement with the expectations.

Table 3. Hydrogen bonds in 6 (distances in Å, angles in °)

O1-H1O1...N12:	O-H 0,73;	H...N 2,12;	O...N 2,839;	O-H...N 168
O1-H2O1...N3:	O-H 0,82;	H...N 1,99;	O...N 2,801;	O-H...N 166
O2-H1O2...N6:	O-H 0,83;	H...N 2,04;	O...N 2,857;	O-H...N 167
O2-H2O2...N9;	O-H 0,80;	H...N 2,05;	O...N 2,823;	O-H...N 164
N13-H13N...O2:	N-H 0,85;	H...O 1,85;	N...O 2,701;	N-H...O 173
N14-H14N...O1:	N-H 0,91;	H...O 1,80;	N...O 2,686;	N-H...O 166

ESCA results of 5

The ESCA spectra (table 4) confirm the basic pattern of the coordination.

- The Pd 3d_{5/2} component points at the Pd(II) state.
- The N 1s peak consists of two components with an intensity ratio of 1:3 (higher-energy:lower-energy), but also a fit with an intensity ratio of 1:2 seems possible. The higher-energy component appears due to the 6 N atoms bound at Pd. The other 12 N atoms contribute to the lower-energy component, leading to a theoretical intensity ratio of 1:2.
- The S 2p peak also consists of two components (doublets) with an intensity ratio of 2:3.5. To the higher-energy component contribute the two bridging atoms in the S bridges Pd1-S3-Pd3 and Pd2-S6-Pd4. The remaining 4 S atoms (S1, S2, S4, S5) coordinating only to one Pd atom resp. contribute to the lower-energy component leading to a theoretical intensity ratio of 1:2.
- The binding energy of Cl 2p_{3/2} points at a chloro ligand. The amount is however twice that of Pd. Possibly this high value is due to a contamination of the sample by not completely separated LiCl.
- The too high amount of carbon results from the contamination of the surface due to the preparation of the sample in the atmosphere.

Table 4 . Binding energies E_b (eV), in brackets half-widths (eV) and relative amounts (atomic %) for 5

Pd3d _{5/2}	338,1 (1,6/2,4)
N1s	399,9 (1,8/8,9); 401,5 (1,9/2,9)
S2p _{3/2}	162,6 (1,6/2,1); 163,6 (1,6/1,2)
Cl2p _{3/2}	198,0 (2,0/5,4)
C1s	285,0 (2,0/70,3); 286,8 (2,0/6,8)

Mass spectra of 5

An exact mass of 2011,91952 was calculated for the tetranuclear Pd complex 5 corresponding to the molecular formula C₈₄H₆₁S₆N₁₈Pd₄Cl₂ (+1; ESI positive mode). The measured high resolution mass spectrum showed a peak at 1975,96490 which corresponds to the molecular

ion minus HCl (hydrogen chlorine probably may be removed at the ion source). For $C_{84}H_{60}S_6N_{18}Pd_4Cl$ (+1) an exact mass of 1976,94338 was calculated. The measured and the simulated spectrum for this mass and the isotopic pattern fit as far as possible.

Infrared (DRIFT) spectrum of 6

The infrared spectrum of 6 diluted by KBr supports the obtained solid state structure (fig. 3).

- Chloroform

The normal mode frequencies at 3036,8 (w, sh), 1221,8 (w), 761,4 (s), and 680,8 (m) cm^{-1} measured in the DRIFT spectrum of 6 agree rather well with the corresponding values of chloroform in the gaseous state (3033; 1205; 760, and 667 cm^{-1})¹⁴. That means, there is nothing to be said against the presence of chloroform within the crystal structure.

- Water

Infrared bands at 3328,4 and 1638,7 cm^{-1} can only be attributed to water stretching vibration (O-HN) and bending vibration (HOH)_{ass}, respectively, because no uncharged species because no uncharged species with N-H bond can occur due to deprotonation of triazole units. In this case, water is associated by O-HN hydrogen bonds.

- Triethylammonium cation

The $(C_2H_5)_3NH^+$ can form hydrogen bonds as well to the oxygen atom of water as to the N atoms of triazole units. Corresponding $\nu(\equiv N-H^+ \dots O, N)$ stretching vibrations should absorb in the region of 2700–2330 cm^{-1} . The band complex with maxima at 2673,1 and 2498,3 cm^{-1} with maxima at 2673,1 and 2498,3 cm^{-1} is broad and therefore consistent with a H-bonding background. However, it cannot be distinguished between N-H---N and N-H---O structures.

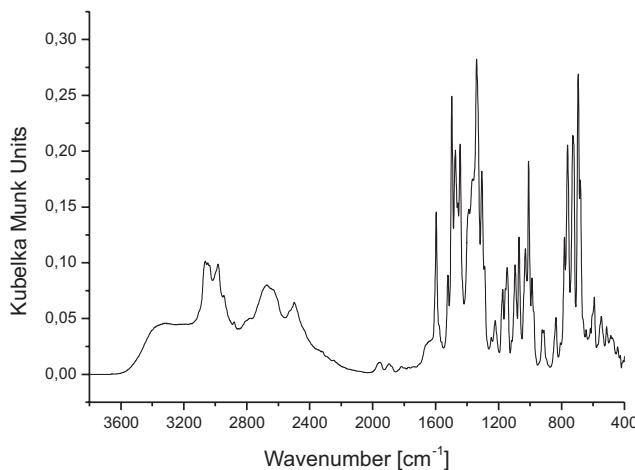


Figure 3. DRIFT spectrum of 6

Table 5. Crystal data and details of structure determinations

	5	6
Empirical formula	$C_{84}H_{60}Cl_2N_{18}Pd_4S_6$	$C_{71}H_{79}Cl_9N_{14}O_2PtS_4$
M_r / g mol ⁻¹	2010,36	1802,86
Colour, habit	red prisms	orange prisms
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a / Å	11,739(2)	14,381(1)
b / Å	15,722(3)	14,718(1)
c / Å	22,906(5)	20,038(1)
α /°	80,460(4)	93,496(3)
β /°	76,242(3)	106,369(3)
γ /°	79,822(4)	97,118(3)
V / Å ³	4007,9(14)	4017,6(3)
Z; F(000)	2; 2008	2; 1828
ρ_{calc} / g cm ⁻³	1,666	1,490
Crystal size / mm	0,31x0,25x0,14	0,21x0,13x0,04
2θ range /°	3,6 – 58,7	6,4 – 56,0
Temperature / K	220	170
$\mu(\text{MoK}\alpha)$ / mm ⁻¹	1,165	2,202
Measured reflections	26288	19210
Unique reflections	18691	19210
Observed reflections (I>2σ(I))	14254	16578
Refined parameters	1027	938
R1 (observed reflections)	0,0386	0,0322
wR2 (unique reflections)	0,0891	0,0862
Largest difference peak and hole / e Å ⁻³	1,05/-0,71	1,82/-1,61

CONCLUSIONS

Two platinum(II) and palladium(II) complexes have synthesized and characterized with 1,2-dihydro-2,5-diphenyl-3H-1,2,4-triazole-3-thion ligand. It is important to highlight that both complexes do not have equal structural behavior. The palladium neutral complex is tetra nuclear, whereas the anionic platinum (II) complex is mononuclear.

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