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Synthesis, characterization and crystal structures of palladium(II) complexes containing neutral, one and twofold deprotonated 1,2,4-triazine species

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ABSTRACT

The synthesis and characterization of three new palladium(II) complexes of 4-amino-6-ethyl-1,2,4-triazine-3-thion-5-one (AETTO, **H_3 L),** $[PdCl_2(\mathbf{H_3}L)]\cdot H_2O$ (**1**), $[Pd_2Cl_2(\mathbf{H_2}L)(PPh_3)_3]NO_3\cdot 2CH_3CN$ (**2**) and $[Pd(\mathbf{HL})(PPh_3)_2]$ (**3**), are reported. All the synthesized compounds are air-stable and were characterized by elemental analyses, IR, NMR spectroscopy and mass spectrometry. In addition, the molecular structures of the complexes have been determined by X-ray single crystal diffraction. On the basis of the crystallographic data, the neutral ligand in **1** and the deprotonated ligands in **2** and **3** act as bidentate NS donors. The singly deprotonated ligand in **2** acts as a bridging agent between two metal centers in the binuclear Pd^{II}-complex.

1. Introduction

The chemistry of compounds containing N and S donor atoms is of special interest since they display a broad spectrum of physicochemical properties and biological activities. The coordination chemistry of such ligands has also attracted considerable attention due to the variety of coordination possibilities associated with them. It is known that metal complexes of biologically active compounds may have enhanced activities compared to the non-coordinated ligands [1–11]. Among the N,S donor ligands, thiosemicarbazide and thiocarbohydrazide and their derivatives constitute an interesting class with enormous biological activities [12–20]. On the other hand, 1,2,4-triazines and their derivatives – as condensation products from the reaction of thiocarbohydrazides with α-keto acids – are well-known compounds. Some of them are found in natural materials, exhibit biological activities and can be used for various purposes since they are associated with diverse pharmacological and biological activities such as analgesic-anti-inflammatory [21–23], antibacterial [24–26], anti-asthmatic [27] and antifungal [28] activities. A variety of synthetic methods are known for the preparation of their substituted derivatives. Metal complexes of 1,2,4-triazine derivatives such as S,N-heterocycles, amino acids and proteins often exhibit enhanced biological activities compared to the uncomplexed ligand [1,29].

The 3-thione substituted derivatives of 1,2,4-triazine can exist in two tautomeric thione (I) and thiol (II) forms (Scheme 1), therefore they can coordinate to metal centers in several fashions, such as a unidentate ligand using the sulfur or nitrogen atom according to the "*Pearson principle*", as a N,S-bidentate chelating agent or as singly deprotonated unidentate or bidentate anions.

Recently, we have reported the behavior of such ligands towards late transition metals such as silver(I), copper(I), copper(II), palladium(II) and platinum(II) ions [30–36]. In our investigations in this research field we have found that 6-aza-2-thiothymine (ATT) – a representative of the 1,2,4-triazine derivatives – acts as a unidentate ligand in methanol/acetonitrile in a 4:1 ratio to form the air-stable complex $[Pd(ATT)_4]Cl_2\cdot 8MeOH$ [33], while 4-amino-6-methyl-1,2,4-triazine-3-thione-5-one (AMTTO), as an another member of the family, acts as a bidentate neutral chelating agent in a 1 + 1 fashion towards palladium(II) halides in the same solvent mixture to give the complexes $[Pd(AMTTO)X_2]\cdot MeOH$ (X = Cl, Br and I) [36]. We have also reported the study of the latter against other nucleophiles like triphenylphosphane [36]. In this communication, we wish to report the results of our studies on the syntheses, characterization and molecular structure of new mono- and binuclear palladacycles containing another representative of this family.

2. Experimental

2.1. General considerations

All chemicals were purchased from Merck and Fluka and were used without further purification. IR spectra were recorded on a

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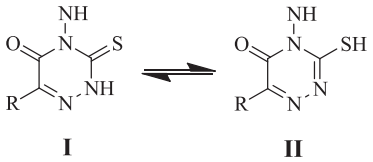


Scheme 1. Thione (I) and thiol (II) tautomeric forms in 3-thione-1,2,4-triazines.

Shimadzu spectrometer 470 (KBr pellets 4000–400 cm^{-1}). Melting points were recorded on a Büchi apparatus B-545 and are uncorrected. The ^{1}H and ^{13}C NMR (**H_3L**) were recorded on a Bruker Avance 500 MHz spectrometer and the ^{31}P NMR spectra were recorded on Bruker 400 MHz and 500 MHz spectrometers using TMS (δ = 0.0 ppm) as the internal standard and 85% aqueous H_3PO_4 as an external standard. Mass spectra were recorded on a Fisons Instruments Trio 1000 spectrometer. Elemental analyses were performed on a Thermo Finigan Flash EA 1112 series elemental analyzer.

2.2. Crystal structure analyses of *H_3L, 1, 2* and *3* (Table 1)

Selected crystals of **H_3L, 1, 2** and **3** were covered with perfluorinated oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and the unit cell dimensions were determined from 2000 (**H_3L**, Stoe IPDS II), 6000 (1, Stoe IPDS I), 10 000 (2, Stoe IPDS II) and 12 000 (3, Stoe IPDS II) reflections (graphite-monochromated Mo Kα radiation (λ = 71.073 pm)). The intensities were corrected for Lorentz and polarizations effects. In addition, absorption corrections were applied for **1**, 2 and **3** (numerical). The structures were solved by direct methods for all compounds using SHELXS-97 for **H_3L** and SIR-92 for the complexes **1**–**3**, they and were refined against F^2 by full-matrix least-squares using the program SHELXL-97. The hydrogen atoms H1–H3 in **H_3L, H2–H5** in **1**, H1 and H2 in **2** and H1 for **3** were freely refined, while the remaining hydrogen atoms in **H_3 L, 1, 2** and **3** were calculated in ideal positions and were refined with a common displacement parameter. The hydrogen atom of the NH-group in **1** was fixed at 85 pm. The programs used were SHELXS-97 [37], SHELXL-97 [38], SIR-92 [39], SHELXTL-PLUS [40] and PLATON [41].

2.3. Synthesis of *H_3L, 1, 2* and *3*

2.3.1. Synthesis of *H_3L*

AETTO was prepared according to a modified literature procedure for the preparation of AMTTO using 2-oxobutyric acid as the α-keto acid [42]. M.p.: 127 °C, *Anal.* Calc. for $C_5H_8N_4OS$ (172.21): C, 34.87; H, 4.68; N, 32.53. Found: C, 34.68; H, 4.70; N, 32.49%. IR (KBr) [ν, cm^{-1}]: 3290 s, 3238 s, 3016 m, 2978 s, 2937 s, 2914 s, 2756 s, 1656 m, 1593 s, 1546 s, 1517 s, 1462 s, 1432 s, 1396 m, 1373 m, 1348 sh, 1309 sh, 1244 s, 1132 m, 1091 s, 968 s, 881 s, 804 s, 711 s, 675 s, 619 s, 569 s, 530 s, 487 s, 443 s, 428 s. MS (70 eV) m/z 172. ^{1}H NMR (δ, $CDCl_3$, 500 MHz): 1.25 (t, J = 7.42 Hz, 3H, CH_3), 2.76 (q, J = 7.42 Hz, 2H, CH_2), 6.20 (br, 2H, NH_2), 10.77 (s, 1H, NH). ^{13}C NMR (δ, $CDCl_3$, 500 MHz): 10.61 (s, CH_3), 24.26 (s, CH_2), 148.92 (C=N), 149.84 (C=O), 169.04 (C=S).

2.3.2. Synthesis of complex *1*

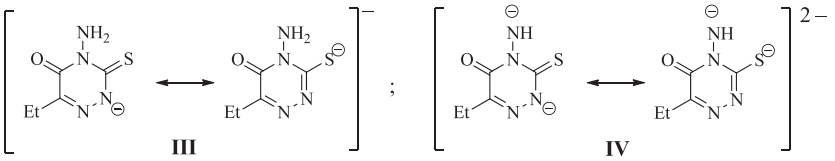
To a solution of **H_3L** (0.17 g, 1 mmol) in methanol/acetonitrile (20 mL, 1:1) was added palladium(II) chloride (0.17 g, 1 mmol), and the reaction mixture was stirred for 5 h at room temperature. After completion of the reaction, which was monitored by TLC using ethyl acetate/petroleum ether (1:2), a yellowish precipitate was filtered off and washed with cold methanol (5 mL). The filtrate was stored at room temperature for one week to yield brownish crystals suitable for X-ray diffraction measurements. Yield: 0.31 g, 90%, m.p.: 258 °C. Elemental analysis: *Anal.* Calc. for $C_5H_8Cl_2N_4OPdS$ (349.53): C, 17.18; H, 2.31; N, 16.03. Found: C, 17.09; H, 2.33; N, 15.99%. IR (KBr) [ν, cm^{-1}]: 3188 w, 2978 w, 2939 m, 2854 m, 2690 m, 2634 m, 2387 m, 2351 m, 2333 m, 1799 w, 1768 w, 1714 s, 1612 s, 1516 m, 1460 w, 1375 w, 1332 s, 1226 m, 1166 w, 1126 vw, 1068 w, 1012 w, 977 w, 918 w, 887 w, 858 w, 715 m, 671 w, 609 vw, 520 m, 490 w, 459 w. EI-MS (30 eV): m/z 278 (Pd(**H_3L**)), 172 (**H_3L**). ^{1}H NMR (δ, DMSO-d_6, 500 MHz): 1.09 (t, J = 7.40 Hz, 3H, CH_3), 2.59 (q, J = 7.40 Hz, 2H, CH_2), 5.90 (s, 1H, NH).

2.3.3. Synthesis of complex *2*

A solution of **H_3L** (0.05 g, 0.3 mmol) in methanol/acetonitrile (1:1, 30 mL) containing sodium acetate (0.02 g, 0.3 mmol) was treated with palladium(II) chloride (0.11 g, 0.6 mmol) and triphenylphosphane (0.23 g, 0.9 mmol) and stirred for 3 h before a solution of silver nitrate (0.05 g, 0.3 mmol) in the same solvent (15 mL) was added. The reaction mixture was stirred for further 3 h. After completion of the reaction, which was monitored by TLC using ethyl acetate and petroleum ether (1:2 v/v) as the eluent, the reaction mixture was filtered off and washed with cold methanol. The filtrate was kept at 4 °C to give yellowish crystals after few weeks. Yield: 0.33 g, 85%, m.p.: 328 °C. Elemental analysis: *Anal.* Calc. for $C_{59}H_{52}Cl_2N_5O_4P_3Pd_2S$ (1303.81): C, 54.35; H, 4.02; N, 5.37. Found: C, 54.20; H, 4.04; N, 5.34%. IR (KBr) [ν, cm^{-1}]: 3421 w, 3051 w, 2970 w, 2929 w, 2875 m, 1685 m, 1633 m, 1435 w, 1381 m, 1361 m, 1240 w, 1163 w, 1095 m, 997 vw, 921 w, 748 s, 694 s, 565 w, 532 s, 511 m, 445 w. EI-MS (30 eV): m/z 277 (Pd(**H_2L**)), 262 (PPh_3), 171 (**H_2L**). ^{1}H NMR (δ, $CDCl_3$ + DMSO-d_6, 500 MHz): 1.16 (t, J = 7.45 Hz, 3H, CH_3), 2.72 (q, J = 7.45 Hz, 2H, CH_2), 7.32–7.65 (m, 15H, 3 PPh_3). ^{31}P NMR (δ, $CDCl_3$, 161.97 MHz): 29.15 (s), 30.10 (s), 32.07.

2.3.4. Synthesis of complex *3*

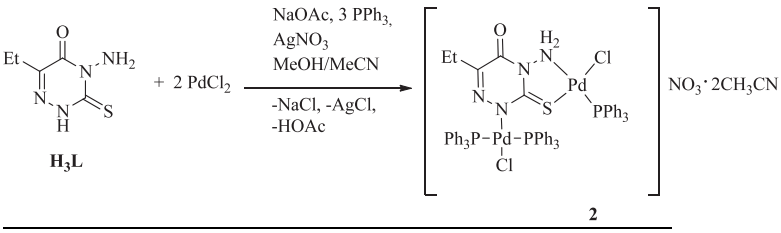
A solution of **H_3L** (0.17 g, 1 mmol) in methanol/acetonitrile (1:1, 30 mL) was treated with sodium acetate (0.16 g, 2 mmol) and stirred for 3 h. To this solution was added [$PdCl_2(PPh_3)_2$] (0.7 g, 1 mmol) under stirring. After 3 h and completion of the reaction, which was monitored by TLC using ethyl acetate and petroleum ether (1:2 v/v) as the eluent, the reaction mixture was filtered off, washed with water (5 mL) and cold methanol (2 × 5 mL). The filtrate was kept at 4 °C to give amber colored crystals after few days. Yield: 0.66 g, 83%, m.p.: 274 °C. Elemental analysis: *Anal.* Calc. for $C_{41}H_{36}N_4OP_2PdS$ (801.14): C, 61.46; H, 4.53; N, 6.99. Found: C, 60.98; H, 4.51; N, 7.01%. IR (KBr) [ν, cm^{-1}]: 3296 m, 3051 m, 2974 w, 2918 m, 2360 w, 1967 w, 1614 s, 1544 m, 1483 m, 1435 s, 1369 m, 1265 s, 1192 w, 1161 w, 1093 m, 1074 w,



Scheme 2. Mesomeric forms of the AETTO-anions.

1055 w, 995 w, 931 w, 846 vw, 746 m, 694 s, 518 s, 455 w, 424 w. EI-MS (30 eV): *m*/*z* 276 (Pd(**HL**)), 262 (PPh_3), 170 (**HL**). ^{1}H NMR (δ, DMSO-d_6): 1.05 (t, J = 7.4 Hz, 3H, CH_3), 2.59 (q, J = 7.4 Hz, 2H, CH_2), 5.90 (s, 1H, NH), 7.31–7.48 (m, 30H, 6Ph). ^{31}P NMR (δ, DMSO-d_6, 202 MHz): 27.65 (br), 28.02 (br).

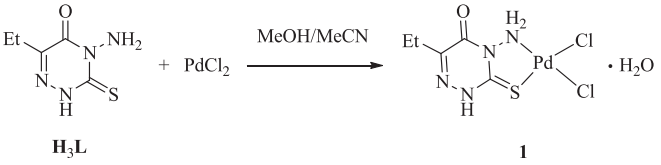
The dinuclear Pd^{II} complex **2** can be obtained by the treatment of **H_3L** with palladium(II) chloride, triphenylphosphane, sodium acetate and silver(I) nitrate in a molar ratio of 1:2:3:1:1 in acetonitrile/methanol, in accordance with Eq. (2).



(2)

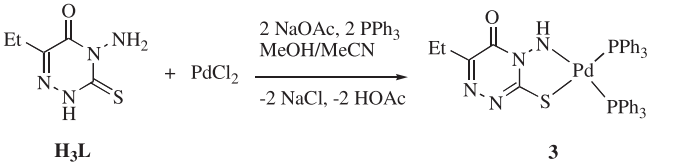
3. Results and discussion

The reaction of **H_3L** with $PdCl_2$ in methanol/acetonitrile gave complex **1** in good yields.



(1)

Complex **3** can be prepared by the reaction of **H_3L** with palladium(II) chloride and triphenylphosphane in the presence of sodium acetate (1:1:2:2) in methanol/acetonitrile, according to Eq. (3).



(3)

Table 1
Crystallographic data for **H_3L** and **1**–**3**.

Compound	**H_3L**	**1**	**2**	**3**
Empirical formula	$C_5H_8N_4OS$	$C_5H_{10}Cl_2N_4O_2PdS$	$C_{63}H_{58}Cl_2N_7O_4P_3Pd_2S$	$C_{41}H_{36}N_4OP_2PdS$
Formula mass	172.21	367.53	1385.83	801.14
Crystal size (mm)	0.12 × 0.11 × 0.04	0.38 × 0.05 × 0.04	0.23 × 0.14 × 0.13	0.17 × 0.04 × 0.03
Crystal system	monoclinic	tetragonal	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{4}2_1c$	$P\bar{1}$	$P2_1/n$
a (pm)	1519.4(1)	1883.6(1)	1247.2(1)	1016.9(1)
b (pm)	666.4(1)	1883.6(1)	1456.4(1)	1936.0(1)
c (pm)	801.0(1)	660.4(1)	1900.5(1)	1843.3(1)
α (°)	90	90	73.19(1)	90
β (°)	103.71(1)	90	83.30(1)	93.48(1)
γ (°)	90	90	65.91(1)	90
Volume [$pm^3 \times 10^6$]	787.93(2)	2343.1(4)	3016.8(4)	3622.2(4)
Z	4	8	2	4
D_{calc} (g cm^{-3})	1.452	2.084	1.526	1.469
Absorption correction	none	numerical	numerical	numerical
μ (cm^{-1}) (Mo Kα)	3.58	22.04	8.53	6.98
Temperature [K]	293(2)	293(2)	100(2)	100(2)
$2\theta_{max}$ (°)	52.26	52.32	51.78	51.86
Index range				
h	−18 → 18	−23 → 21	−15 → 15	−12 → 11
k	−8 → 8	−23 → 20	−17 → 17	−23 → 23
l	−9 → 9	−8 → 8	−23 → 23	−22 → 22
Reflections collected	5314	10267	42920	27273
Unique reflections (R_{int})	1503 (0.0692)	2312 (0.0471)	11700 (0.0495)	6900 (0.0755)
Reflections with $F_o > 4\sigma(F_o)$	796	1712	8539	4424
Parameters	120	161	740	455
Flack parameter	–	0.01(6)	–	–
R_1	0.0613	0.0325	0.032	0.0334
wR_2 (all data)	0.1623[a]	0.0604[b]	0.0731[c]	0.0514[d]
Maximum residual electron density ((e pm^{-3}) × 10^{-6})	0.18	0.601	0.855	0.36

[a] $w = 1/[\sigma^2(F_o^2) + (0.0685P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.0273P)^2]$.
[c] $w = 1/[\sigma^2(F_o^2) + (0.0427P)^2]$.
[d] $w = 1/[\sigma^2(F_o^2) + (0.0138P)^2]$.

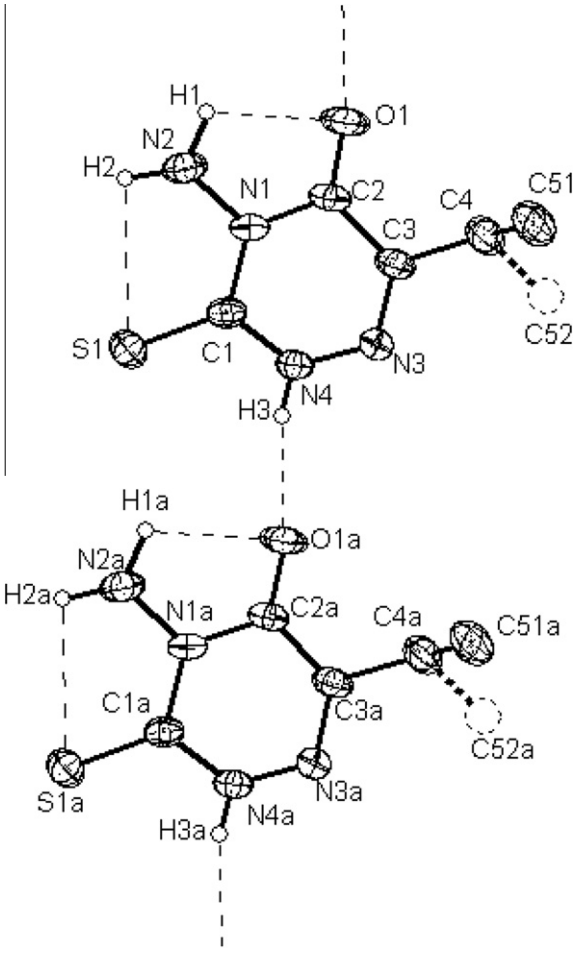


Fig. 1. Molecular structure of H_3L (thermal ellipsoids at the 30% probability level). Selected bond lengths [pm] and angles [°]: S1–C1 164.8(5), O1–C2 121.5(5), N1–C2 137.9(6), N1–C1 138.4(6), N1–N2 141.3(6), N3–C3 130.0(6), N3–N4 133.5(5), N4–C1 136.7(6), C4–C52 137(1), C4–C51 146(1); C2–N1–C1 124.6(4), C2–N1–N2 117.9(4), C1–N1–N2 117.4(4), C3–N3–N4 116.6(4), N3–N4–C1 129.4(4), C52–C4–C3 117.6(7), C51–C4–C3 116.5(7).

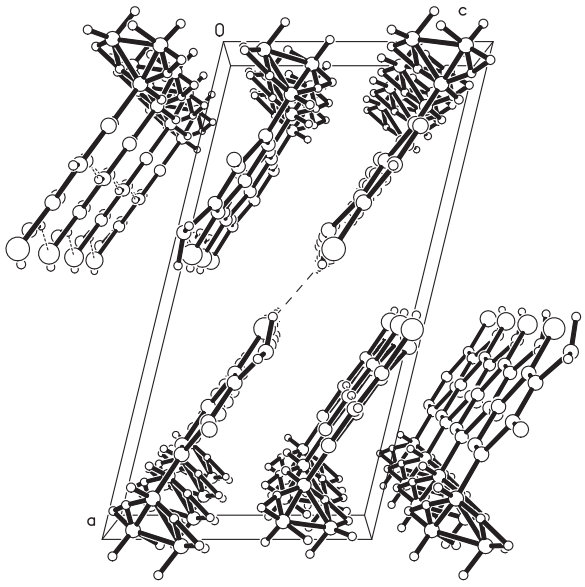


Fig. 2. The packing diagram for H_3L.

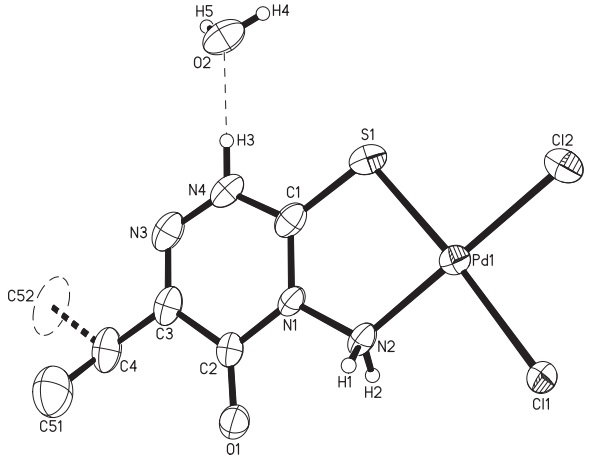


Fig. 3. Molecular structure of **1** (thermal ellipsoids at the 40% probability level). Selected bond lengths [pm] and angles [°]: Pd1–N2 202.0(5), Pd1–S1 224.7(2), Pd1–Cl2 228.8(2), Pd1–Cl1 232.3(2), S1–C1 169.7(6), N1–C1 135.7(7), N1–C2 140.3(8), N1–N2 143.0(6), N3–C3 129.8(9), N3–N4 135.2(8), N4–C1 132.9(7), O2–H4 81(8), O2–H5 78(9); N2–Pd1–S1 87.3(1), N2–Pd1–Cl2 178.5(2), S1–Pd1–Cl2 92.08(7), N2–Pd1–Cl1 88.4(1), S1–Pd1–Cl1 175.68(6), Cl2–Pd1–Cl1 92.23(6), C1–S1–Pd1 97.2(2), N1–N2–Pd1 114.8(3), H4–O2–H5 97(8).

In contrast to Eq. (1), the reactions according to Eqs. (2) and (3) give complexes **2** and **3** incorporating the anionic ligands III and IV (Scheme 2). This result is obtained by abstraction of one HCl molecule from **2** and two HCl molecules from **3** by the sodium acetate as a base. The coordination of the sulfur atom leads to additional acidification of the amine functions, as shown in Scheme 2. Furthermore, the reaction mixture of Eq. (2) undergoes a chloride–nitrate anion exchange reaction in the presence of silver(I) nitrate.

Complexes **1**–**3** were found to be air-stable crystalline solids. In accordance with the structures of the compounds, the ^{31}P NMR spectrum of **2** in $CDCl_3$ exhibit three signals at $\delta = 29.15$, 30.10 and 32.07 ppm and the ^{31}P NMR spectrum of **3** in DMSO-d_6 show

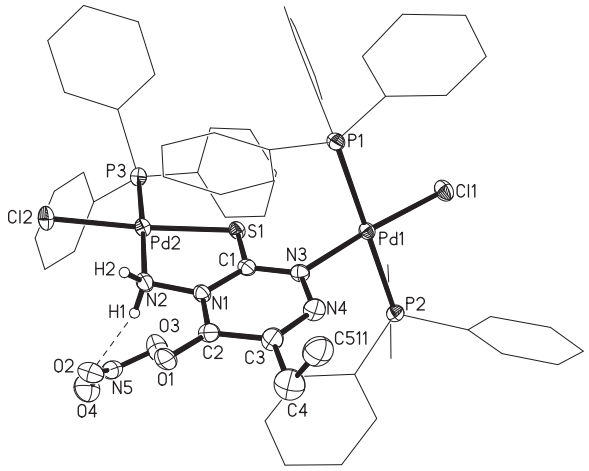


Fig. 4. Molecular structure of **2** (thermal ellipsoids at the 40% probability level, most of hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: Pd1–N3 202.8(2), Pd1–Cl1 229.97(8), Pd1–P2 232.90(9), Pd1–P1 238.39(9), Pd2–N2 210.3(3), Pd2–P3 223.87(9), Pd2–S1 227.43(8), Pd2–Cl2 232.22(8), S1–C1 171.7(3), O1–C2 121.6(4), N1–C1 136.6(4), N1–C2 139.4(4), N1–N2 143.0(4), N3–C1 132.0(4), N3–N4 137.3(3), N4–C3 129.0(4), N5–O3 1.240(4), N5–O4 1.245(4), N5–O2 1.257(4); N3–Pd1–Cl1 175.84(8), N3–Pd1–P2 90.07(8), Cl1–Pd1–P2 87.02(3), N3–Pd1–P1 90.62(8), Cl1–Pd1–P1 92.38(3), P2–Pd1–P1 178.13(3), N2–Pd2–P3 177.14(9), N2–Pd2–S1 85.63(7), P3–Pd2–S1 96.02(3), N2–Pd2–Cl2 91.11(7), P3–Pd2–Cl2 87.54(3), O3–N5–O4 120.3(3), O3–N5–O2 119.5(3), O4–N5–O2 120.2(3).

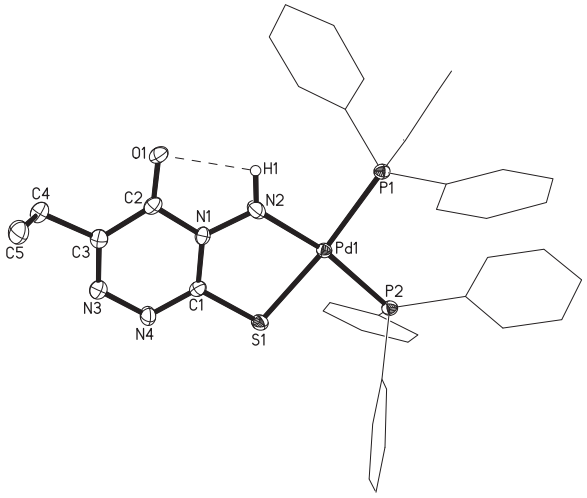


Fig. 5. Molecular structure of **3** (thermal ellipsoids at the 40% probability level, most of hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: Pd1–N2 199.2(3), Pd1–P1 230.22(8), Pd1–P2 230.73(8), Pd1–S1 230.73(8), S1–C1 173.7(4), O1–C2 123.2(4), N1–C1 134.9(4), N1–C2 139.8(4), N1–N2 137.1(4), N3–C3 130.8(4), C1–N4 133.2(4); N2–Pd1–P2 170.46(9), N2–Pd1–P1 90.96(9), P1–Pd1–P2 98.38(3), N2–Pd1–S1 83.60(9), P2–Pd1–S1 87.09(3), S1–Pd1–P1 174.40(4), C1–S1–Pd1 98.40(1).

two broad signals at δ = 27.65 and 28.02 ppm, indicating the non-equivalence of the phosphorus atoms as consequence of the asymmetric S,N coordination of the **HL** ligand. In the IR spectra of **1**–**3**, the observed absorptions at 459 cm^{-1} for **1**, 445 cm^{-1} for **2** and 455 cm^{-1} for **3** can be assigned to Pd–N vibrations [43]. C=O– and C=N– vibrations can be observed as two bands at 1656 and 1593 cm^{-1} for $\mathbf{H_3L}$, at 1714 and 1612 cm^{-1} for **1**, at 1685 and 1633 cm^{-1} for **2** and at 1614 and 1544 cm^{-1} for **3**. The P–C vibrations of PPh_3-moiety are observed in the range 748–694 cm^{-1} for **2** and 746–694 cm^{-1} for **3**. Each IR spectra exhibit two bands for the valence vibrations for the NH_2-groups at 3290 and 3238 cm^{-1} ($\mathbf{H_3}$L), 3250 and 3188 cm^{-1} (**1**), 3296 and 3251 cm^{-1} (**2**), while the spectrum of **3** shows only one absorption at 3296 cm^{-1} as consequence of the deprotonation of the NH_2 moiety in **3**. The mass spectra of the complexes recorded at 70 eV showed only the signals of the corresponding ligands in **1**–**3** (m/z = 172 (**1**), m/z = 171 (**2**) and m/z = 170 (**3**)) and the signal of the triphenylphosphane moiety for **2** and **3** at m/z = 262, while the spectra recorded at a lower voltage (30 eV) showed additionally new signals at m/z = 278 (**1**), m/z = 277 (**2**) and m/z = 276 (**3**), which can be assigned to the corresponding PdL-fragmentations of the complexes.

Table 1 shows the crystallographic data of the compounds and Figs. 3–5 illustrate the molecular structures of complexes **1**, 2 and **3**, respectively.

3.1. Crystal structures of compound $\mathbf{H_3L}$, 1, 2 and 3

3.1.1. Compound $\mathbf{H_3L}$

Compound $\mathbf{H_3L}$ crystallizes in the monoclinic space group $P2_1/c$. The basic six-membered ring skeleton in this compound is planar (Fig. 1). The bond distances in the triazine six-membered heterocycle are in good agreement with those observed in AMTTO [44]. The ethyl group is disordered with an occupancy factor of 0.5:0.5 for C51:C52. The S1–C1 bond length in $\mathbf{H_3L}$ with a mean value of 164.8(5) pm is significant for high double bond character. In $\mathbf{H_3L}$, the NH_2-group of each ligand is linked to the sulfur and oxygen atoms *via* weak intramolecular hydrogen bondings (N2–H1···O1: 298.0(6) pm and N2–H1–O1: 109(7)°, N2–H2···S1: 267.0(6) pm and N2–H2–S1: 99(6)°), while the NH-group links to the oxygen atom of the adjacent molecule *via* hydrogen bonding (N4–H3···O1a: 282.0(6) pm and N4–H3–O1a: 162(7)°). The latter is responsible for the formation of double-layers parallel to (1 0 0) (Fig. 2). There are weak hydrogen bonds between the packed molecules in the double-layers, whose "edges" are shielded with the disordered ethyl-tail.

3.1.2. Complexes 1, 2 and 3

Complexes $[PdCl_2(\mathbf{H_3}L)]\cdot H_2O$ (**1**, Fig. 3) and $[Pd(\mathbf{HL})(PPh_3)_2]$ (**3**, Fig. 5) are neutral molecules, whereas complex **2** consist of $[(PPh_3)_2ClPd(\mathbf{H_2}L)Pd(PPh_3)Cl]^+$-cations and nitrate anions (Fig. 4). The structural data of the complexes show that **1** incorporates $\mathbf{H_3L}$ in its neutral form, while the corresponding ligands in **2** and **3** are mono and twofold deprotonated AETTO moieties, respectively.

In all the complexes **1**–**3**, the corresponding ligand acts as chelating and coordinates to the metal center *via* its sulfur and hydrazine nitrogen donors in a κ^2-N,S-coordination mode, forming a five-membered chelate ring. In the case of complex **2**, the singly deprotonated AETTO-ligand coordinates additionally to a second metal ion through one of its endocyclic nitrogen atoms (κ^1-N-coordination mode). The square planar geometry around the metal centers in **1** and **3** are completed by two chlorine atoms

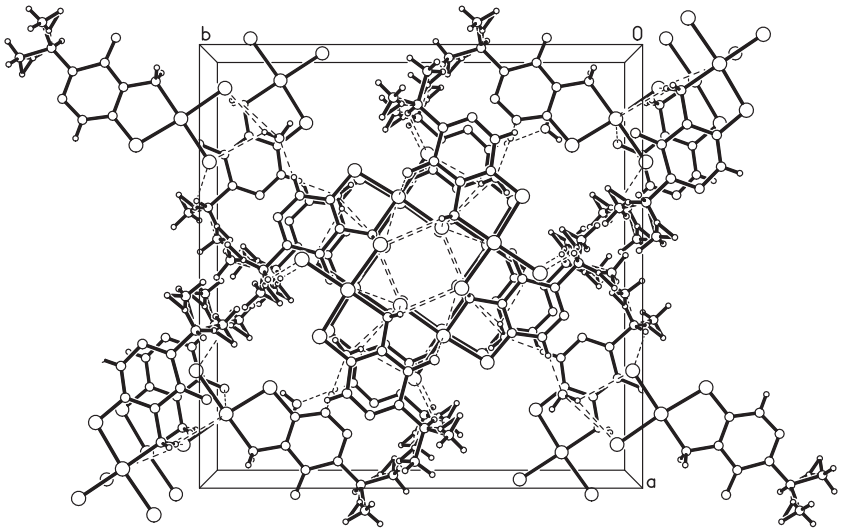


Fig. 6. The packing diagram of **1** involving hydrogen bonding.

and two triphenylphosphane molecules, respectively. The square planar arrangement about the palladium centers in **2** is completed by one chloride ligand and two *trans*-positioned triphenylphosphane molecules for Pd1 and one triphenylphosphane molecule and one chloride ligand for Pd2. The latter is oriented *cis* to the amine group of the heterocycle, indicating the strong influence of the π-acids C=S and PPh_3. A similar coordination mode is observed in the tetrameric palladium(II) complex $[Pd(L)]_4{\cdot}2C_7H_8$, where L is the twofold deprotonated Schiff-base (E)-4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one [45].

The graphical representation of **1** (Fig. 3) shows, except for the disordered ethyl group (occupancy factor 0.65:0.35 for C51:C52), a basically planar framework.

The Pd–Cl distances in **1** (232.3(2) and 228.8(2) pm) and those in **2** (229.97(8) and 232.22(8) pm) are very similar to those in $[Pd(AMTTO)Cl_2]{\cdot}CH_3OH$ (232.2(2) and 228.9(1) pm) [44] and $[Pd(AMTTO)Cl(PPh_3)]Cl{\cdot}CH_3OH$ (231.14(6) pm) [46]. The strong *trans*-influence of the sulfur atoms in comparison with the nitrogen atom is responsible for the observed differences in the Pd–Cl distances.

The $Pd–N_{hydrazine}$ bond lengths of 202.0(5) pm (**1**) and 210.3(3) pm (**2**) compare well to those found in the AMTTO-palladacycle and in the other palladium(II)–nitrogen–sulfur complexes [30–36,44–50]. The observed Pd–N bond length of 199.2(3) pm in **3** is somewhat shorter than those in **1** and **2**. This bond shortening is attributed to the change in the hybridization of nitrogen atoms as a consequence of the deprotonation. A similar Pd–N bond length (202.8(2) pm) is also observed for the sp^2-hybridized endocyclic nitrogen atom in **2**. Due to the stronger *trans*-influence of the triphenylphosphane moieties compared with chloride, the Pd–S bond distances in **1** and **2** are slightly shorter than the observed one in **3** (224.7(6) pm (**1**), 227.43(8) pm (**2**) and 230.73(8) pm (**3**)).

The Pd–P bond lengths of 223.87(9), 232.90(9) and 238.39(9) pm (**2**) and 230.22(8) and 230.73(8) pm (**3**) are shorter than the sum of the single bond radii for palladium and phosphorus, i.e. 241 pm [51] and fall in the wide range (221–246 pm) of $Pd^{II}–PPh_3$ bond reference values (average 230.2 pm) encountered in 248 entries [52]. The presence of the $\mathbf{H_2L}$ ligand in **2** and **HL** ligand in **3** leads only to marginal differences in the bonding parameters due to the delocalization of the charge in III and IV, as shown in Scheme 2.

In the molecular structure of **1**, one solvate molecule (water) is bound to the endocyclic NH-group *via* a hydrogen bridge (N4···O2d: 271.2(7) pm). **1** is fixed in a network of hydrogen bridges, which is formed between the amine group of the heterocycle, the oxygen atom of the solvate molecule and the halide atoms of adjacent complexes (N2···Cl1a: 330.5(6) pm, N2···Cl2b: 332.2(6) pm, N2···Cl1c: 332.2(6) pm, O2···Cl1e: 319.4(7) pm and O2···Cl1f: 329.2(7) pm) (Fig. 6).

In **2**, the NH_2 group of one cation acts as a bridging agent between one oxygen atom of a nitrate anion and the oxygen atom of an adjacent cation using both its hydrogen atoms *via* hydrogen bridges (N2–H1···O2: 279.7(4) pm and N2–H1–O2: 150(4)°, N2–H2···O1a: 271.3(4) pm and N2–H2–O1a 161(4)°). This coordination mode is responsible for the formation of a one dimensional chain along [0 0 1]. The dihedral angle between the "best" planes in **2** (A: Pd1/Cl1/N3/P1/P2, B: Pd2/Cl2/S1/N2/P3 and C: N1/N3/N4/C1/C2/C3) are 112° (A, B), 107° (A, C) and 12° (B, C).

There is an intramolecular hydrogen bridge between the exocyclic NH-group and the carbonyl oxygen moiety (N2–H1···O1: 266.1(4) pm).

4. Conclusion

In conclusion, we have synthesized and characterized two mononuclear and one binuclear complex containing neutral, mono and twofold deprotonated AETTO. To our knowledge, among the palladacycles containing 4-amino-6-alkyl/aryl-1,2,4-triazine-3-thione as a ligand, complex **3** is the first example having a twofold deprotonated species. Due to the determined molecular structures of the complexes, the corresponding ligand acts as bidentate N,S-chelating one to the metal centers. In the case of the binuclear complex, the singly deprotonated triazine moiety acts as a bridge between two metal centers *via* its endocyclic nitrogen atom.

Appendix A. Supplementary data

CCDC 712072, 712073, 712074 and 773397 contains the supplementary crystallographic data for compounds $\mathbf{H_3L}$, **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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