Inorganica Chimica Acta 443 (2016) 160-169

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Square planar Pd(II) complexes derived from 1-ethyl-3-phenylthiourea, 3-mercapto-4-methyl-1,2,4-triazole and 2-mercapto-5-methyl-1,3, 4-thiadiazole: Syntheses, spectral, structural characterization and photoluminescence properties



P. Bharati^a, A. Bharti^b, P. Nath^a, S. Kumari^a, N.K. Singh^a, M.K. Bharty^{a,*}

^a Department of Chemistry, Banaras Hindu University, Varanasi 221005, India ^b Department of Chemistry, Kirori Mal College, University of Delhi, Delhi 110007, India

ARTICLE INFO

Article history: Received 28 October 2015 Received in revised form 31 December 2015 Accepted 2 January 2016 Available online 7 January 2016

Keywords: Thiadiazole and triazole complexes Pd(II) complexes Square planar complexes Photoluminescence properties

ABSTRACT

The reaction of PdCl₂ with 1-ethyl-3-phenyl-thiourea (Heptu), 3-mercapto-4-methyl-4H-1,2,4-triazole (Hmmtrz) and 2-mercapto-5-methyl-1,3,4-thiadiazole (Hmthd) respectively, yielded three new complexes [Pd(eptu)₂] (**1**), [Pd(Hmmtrz)₄]Cl₂ (**2**) and [Pd(Hmthd)₄]Cl₂·2CHCl₃ (**3**). These complexes have been isolated in pure form and characterized by elemental analyses, IR, NMR and single crystal X-ray diffraction technique. In all compounds the metal ion adopts a square-planar geometry. Two nitrogen and two sulfur atoms from the monoanionic eptu ligand in complex **1** are bonded to Pd(II) centre in *trans* fashion. Complexes **2** and **3** are salt-like and the metal centre is bonded through four neutral ligands. The electrical neutrality in these complexes is maintained by the presence of two chlorides as counter ions. Migration of hydrogen, within the ligand framework in complexes **2** and **3**, from sulfur to nitrogen is observed that resulted in the thione form of the ligand and its coordination to the metal centre in both the complexes. Complexe **2** is stabilized by intermolecular C-H···N and intramolecular N-H··CI hydrogen bonding leading to an extended structure. Complex **3** is stabilized by intermolecular C-H···S hydrogen bonding. Complexes **1–3** are fluorescent materials which upon excitation at 31000, 38600 and 32300 cm⁻¹ exhibit an emission at 25200, 27000 and 26700 cm⁻¹, respectively.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The coordination behavior of thiourea and its derivatives have been reported during last few decades [1–4]. Substituted thioureas exhibit efficient capacity for coordination with transition metals producing interesting colored compounds. Thioureas act as analytical reagents, for the determination of metals in the presence of other metal ions [5,6]. N,N'-Substituted thioureas may show different bonding possibilities (Scheme 1). They may act as monoanionic monodentate ligand binding through thiolato sulfur atom (I), as neutral monodentate bonded through thione sulfur atom (II), dianionic N,S bidentate ligand binding through sulfur and nitrogen atoms (III) or as dianionic N,S bidentate ligand in dinuclear complexes involving sulfur bridging (IV). They can also act as neutral bridging ligand through the sulfur atom (V). Other bonding possibilities of substituted thioureas may be mononegative tridentate form that utilize thiolato form to form bridges between M–M bonded trinuclear centres (VI and VII) (Scheme 1) [7–10]. Unsymmetrically substituted thiourea RNH(C=S)NHR', because of the presence of one NH group on each side of (C=S) moiety, may exhibit two tautomeric forms *viz*. RN = C(SH)NHR' and RNHC(SH) = NR' [11,1]. Thus, they may act as hard and soft donor providing a multitude of bonding possibilities.

Mercapto-triazoles are important ligands with nitrogen-sulfur donor centres which produce supramolecular network with novel topologies [12–16]. Two types of mercapto-triazoles are found in the literature, 1,2,3 and 1,2,4-triazoles exhibit different bonding behaviour. They act as bidentate-bridging or monodentate ligands depending on the position and the nature of the substituent at the triazole ring [17]. The N1 and N2 positions of the triazole ring if not substituted may coordinate to the metal ion forming N1, N2 bridging polynuclear complexes [18–20]. The mercapto group (thiol form) can also function as a donor site exhibiting uninegative monodentate or neutral bridging modes between two metal centres or as a bridge between three metal centres in the azolato or thiolato form. Studies on thiadiazole and its derivatives, which belong to an important group of nitrogen sulfur donor ligands, are the major

^{*} Corresponding author. Tel.: +91 5426702447; fax: +91 0542 2368127. *E-mail address:* mkbharty@bhu.ac.in (M.K. Bharty).



Scheme 1. Bonding possibilities of 1-ethyl-3-phenylthiourea (Heptu) in its neutral, monoanionic and dianionic forms involving thiol-thione tautomers.

area of research because of their diverse biological activities, such as anti-tubercular, anti-inflammatory, analgesic, antipyretic, anticonvulsant, antibacterial and antifungal [21–26]. Triazole and thiadiazole ligands can exist in tautomeric equilibrium in solution, which enables two possible configurations of the --NHCS moiety as thione and thiol forms (Scheme 2). On complexation with ring nitrogen, only the thione form of the ligands exists in the solidstate. This tautomerism may cause the proton transfer or migration on the triazole/thiadiazole ring, and consequently the ligand binds in various modes with different metal ions (Scheme 3) [27,28]. Palladium complexes show high efficiency as homogenous catalysts in a variety of coupling reactions in organic synthesis [29-33]. Pd (II) complex of a triazole-based ligand has been reported as a catalyst for the Heck reaction [34]. Pd(II) complexes with 1,3-bis (2'-imidazolinyl)benzene have high catalytic activity in the Friedel-Crafts alkylation reaction [35]. Pd(II) complex of thioamide ligand, 2,6-bis(butylaminothio-carbonyl)pyridine is considered to be efficient catalysts for Negishi coupling reaction [36]. In view of the above interesting coordination behaviour of the nitrogensulfur ligands and catalytic nature of palladium(II) complexes, we have synthesized and fully characterized three new palladium(II) complexes, $[Pd(eptu)_2]$ (1), $[Pd(Hmmtrz)_4]Cl_2$ (2) and [Pd(Hmthd)₄]Cl₂·2CHCl₃ (**3**) from 1-ethyl-3-phenylthiourea (Heptu), 3-mercapto-4-methyl-4H-1,2,4-triazole (Hmmtrz) and 2-mercapto-5-methyl-1,3,4-thiadiazole (Hmthd), respectively.

2. Experimental

2.1. Chemicals and starting materials

The ligands, 3-mercapto-4-methyl-4H-1,2,4-triazole (Hmmtrz) and 2-mercapto-5-methyl-1,3,4-thiadiazole (Hmthd) were





purchased from Sigma Aldrich. The ligand, 1-ethyl-3-phenylthiourea (Heptu) was prepared by the literature method [37]. Other chemicals were of reagent grade and used as purchased without further purification. All the synthetic manipulations were carried out in open atmosphere at room temperature. The solvents were distilled before use following the standard procedure.

2.2. Physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were measured on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erba 1108 instrument. Infrared spectra (IR) were recorded in the 4000–400 cm⁻¹ region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in DMSO-d₆ and CDCl₃ on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference. The emission and excitation spectra were recorded at ambient temperature with a Varian Cary Eclipse spectrophotometer in CHCl₃ solution.

2.3. Synthesis of $[Pd(eptu)_2](1)$

PdCl₂ (0.177 g, 1 mmol) was added to a solution of Heptu (0.360 g, 2 mmol) in 10 mL methanol–chloroform mixture and stirred for 12 h at room temperature. A clear red solution was obtained which was filtered off and kept for crystallization. Block-shaped crystals suitable for X-ray analysis were obtained. Yield: 70%; m.p. 199 °C. *Anal.* Calc. for C₁₈H₂₂N₄PdS₂ (464.94): C, 46.45; H, 4.73; N, 24.08, S, 13.76; Found: C, 46.49; H, 4.69; N, 24.06; S, 13.74%. IR (ν cm⁻¹, KBr): ν (NH) 3121; ν (C=N) 1556; ν (C=S) 901; ν (N–N) 1099; ν (Pd–S) 541; ¹H NMR (CDCl₃; δ ppm): 11.06 (s, 2H, NH), 7.64–6.73 (m, 10H, aromatic protons), 4.49 (q, 4H, CH₂), 1.30 (t, 6H, CH₃). ¹³C NMR (CDCl₃; δ ppm): 179.55 (C=S), 141.70–123.15 (aromatic carbons), 63.85 (CH₂), 14.21 (CH₃). UV–Vis. [CHCl₃, λ_{max} , nm; ε_{max} , M⁻¹ cm⁻¹]: 245 (1.14 × 10⁵), 278 (7.0 × 10⁴), 323 (3.8 × 10⁴).

2.4. Synthesis of $[Pd(Hmmtrz)_4]Cl_2(2)$

A mixture of chloroform suspension (10 mL) of $PdCl_2$ (0.177 g, 1 mmol) and methanol solution of Hmmtrz (0.461 g, 4 mmol) was stirred for 6 h at room temperature. An orange-red solution was obtained, which was filtered off and kept for crystallization.



 $X = S; R = CH_3$ (Hmthd)

Scheme 3. Possible bonding modes of Hmmtrz and Hmthd ligands.

Upon slow evaporation of the solvents, orange-red crystals suitable for X-ray analysis were obtained after 20 days. Yield: 50%; m.p. 145 °C. *Anal.* Calc. for $C_{12}H_{20}Cl_2N_{12}PdS_4$ (637.94): C, 22.57; H, 3.13; N, 26.33; S, 20.06; Found: C, 22.60; H, 3.10; N, 26.31; S, 20.02%. IR (ν cm⁻¹, KBr): ν (N–H) 3121, ν (C–H) 2944–3019; ν (C=N) 1556; ν (N–N) 1079 s; ν (C–S) 782; ν (Pd–S) 541; ¹H NMR (CDCl₃; δ ppm): 13.44 (s, 4H, NH), 7.91 (s, 4H, CH, triazole ring proton), 3.58 (s, 12H, CH₃). ¹³C NMR (CDCl₃; δ ppm): 166.75 (NCS), 140.93 (aromatic carbons), 31.53 (CH₃ carbon). UV–Vis. [CHCl₃, λ_{max} , nm; ε_{max} , M⁻¹ cm⁻¹]: 259 (9.0 × 10⁴).

2.5. Synthesis of [Pd(Hmthd)₄]Cl₂·2CHCl₃ (**3**)

To a methanol solution (15 mL) of Hmthd (0.468 g, 4 mmol) was added a methanol-chloroform suspension (10 mL) of PdCl₂ (0.177 g, 1 mmol) and stirred for 10 h at room temperature which yielded an orange-red solution. This was filtered off and kept for crystallization. Upon slow evaporation of the solvents at room temperature, rod-shaped crystals were obtained after 30 days. Yield: 60%; m.p. 183 °C. *Anal.* Calc. for C₁₄H₁₈Cl₈N₈PdS₈ (944.84): C, 17.78; H, 1.90; N, 11.85; S, 27.09; Found: C, 17.82; H, 1.49; N, 11.92; S, 27.19%. IR (ν cm⁻¹, KBr): ν (N–H) 3052, ν (C–H) 2973; ν (C=N) 1554; ν (C–S) 766; ν (N–N) 1066s; ν (Pd–S) 432; ¹H NMR (DMSO-d₆; δ ppm): 13.96 (s, 4H, NH); 7.59 (s, 2H, CHCl₃), 3.37 (s, 12H, CH₃). ¹³C NMR (DMSO-d₆; δ ppm): 188.90 (C–S), 158.47 (C–N), 77.46 (carbon of CHCl₃), 15.89 (CH₃ carbon). UV–Vis. [CHCl₃, λ_{max} , nm; ε_{max} , M⁻¹ cm⁻¹]: 310 (8.7 × 10⁴).

2.6. X-ray crystallography

Structural measurements of complexes **1**, **2** and **3** were performed on a computer-controlled Oxford Gemini diffractometer equipped with a CrysAlis CCD software using a graphite monochromated Mo K α (λ = 0.71073 Å) radiation source at 293 K. Multi-scan absorption correction was applied to the X-ray data collection for all the compounds. The structures were solved by direct methods (SHELXS-08) and refined against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model [38]. The MERCURY package and ORTEP-3 for Windows program were used for generating molecular graphics [39,40].

3. Results and discussion

The ligand, 1-ethyl-3-phenyl-thiourea (Heptu) reacts with palladium(II) chloride to form orange-red complex, $[Pd(eptu)_2]$ (1) in methanol-chloroform solution. The ligand 3-mercapto-4methyl-4H-1,2,4-triazole reacts with PdCl₂ to yield orange-red precipitate of $[Pd(Hmmtrz)_4]Cl_2$ (2) which was dissolved upon addition of chloroform. Similarly, 2-mercapto-5-methyl-1,3, 4-thiadiazole affords a mononuclear complex, $[Pd(Hmthd)_4]$ Cl_2 ·2CHCl₃ (3) with a distorted square planar geometry at Pd(II) centre utilizing four neutral monodentate ligands. Complexes 2 and **3** are salt-like, contain two chlorides as counter ions and the ligands coordinate in the neutral form. Similar complexes have been reported in the literature [41,42]. Schemes 4–6 depict formation of the complexes which also show that the thiourea ligand acts as monoanionic N,S bidentate chelating ligand while 3-mercapto-4-methyl-4H-1,2,4-triazole and 2-mercapto-5-methyl-1,3,4-thiadiazole coordinate in the thione form after the migration of proton from S to N during complex formation. Complexes **1**, **2** and **3** are soluble in chloroform and melt at 199, 145 and 183 °C, respectively.

3.1. Magnetic moments and electronic spectra

The complexes $[Pd(eptu)_2]$ (1), $[Pd(Hmmtrz)_4]Cl_2$ (2) and $[Pd(Hmthd)_4]Cl_2 \cdot 2CHCl_3$ (3) are diamagnetic indicating the presence of low spin Pd(II) centres. They show absorptions in the region of $31000-33300 \text{ cm}^{-1}$ due to intraligand/charge transfer transitions characteristics of low spin d⁸ Pd(II) complexes with square planar geometry [43]. The complex 1 shows three bands at 40800, 36000 and 31000 cm⁻¹ while complexes 2 and 3 show only one band at 38600 and 32300 cm⁻¹, respectively. The three bands observed in complex 1 are assigned to $\pi \to \pi^*$ (C=S) and $n \to \pi^*$ transitions while the bands in complexes 2 and 3 are attributed to the $\pi \to \pi^*$ transition of C=S group [44].

3.2. IR spectra

The IR spectrum of the ligand 1-ethyl-3-phenyl-thiourea (Heptu) shows bands at 3215 and 3117 cm⁻¹, due to v(NH), and a band at 956 cm⁻¹ for v(C=S). Presence of a band at 3121 cm⁻¹ due to v(NH) in the spectrum of complex **1** indicates the presence of an NH group adjacent to the ethyl group which does not take part in bonding. However, the disappearance of the v(NH) band around 3215 cm⁻¹ suggests loss of the thioamide proton adjacent to the phenyl group and participation of the deprotonated



Scheme 4. Synthesis of [Pd(eptu)₂] (1) complex.



Scheme 5. Synthesis of [Pd(Hmmtrz)₄]Cl₂ (2) complex.



Scheme 6. Synthesis of [Pd(Hmthd)₄]Cl₂·2CHCl₃ (3) complex.

thioamide nitrogen in bonding with the metal ion. The band due to v(C=S) suffers a negative shift of 55 cm⁻¹ suggesting bonding of the ligand *via* the thioamide sulfur to the metal ion [37]. The ligand adopts thione form in the complex which is supported by the presence of v(N=H) at 3121 cm⁻¹. The thione form of the ligand is supported by the occurrence of v(C=S) and v(Pd=S) at 852 and 541 cm⁻¹, respectively. The ligand 2-mercapto-5-methyl-1,3, 4-thiadiazole shows bands at 2868 and 1554 cm⁻¹ due to v(SH) and v(C=N), respectively. The IR spectrum of complex **3** shows absence of the v(SH) band and appearance of v(NH) at 3052 cm⁻¹, indicating bonding through the thione sulfur after tautomerization during the complex formation. The coordinated ligand adopts the thione form as supported by the occurrence of stretching vibrations of C=S and Pd-S at 766 and 432 cm⁻¹, respectively.

3.3. ¹H and ¹³C NMR spectra

The ¹H NMR spectrum of free Heptu ligand exhibits signals at δ 11.06 and 4.49 ppm for the NH protons attached to the ethyl group and phenyl ring, respectively. The phenyl ring protons appear as a multiplet in the region δ 7.11–7.64 ppm. The –CH₂ and –CH₃ protons of the ethyl group appear at δ 2.49 and 1.32 ppm, respectively. The ¹H NMR spectrum of the complex [Pd(eptu)₂] (**1**) shows the absence of a signal for the –NH proton attached to the phenyl ring, while the –NH proton attached to ethyl group appears at δ 11.06 ppm, indicating that the metal is bonded to the ligand *via* the nitrogen atom attached to the phenyl ring after loss of a proton. The ¹³C NMR spectrum of [Pd(eptu)₂] (**1**) shows signals at 179.55, 63.85 and 14.21 ppm due to C=S, CH₂ and CH₃ carbons, respectively. The ¹H NMR spectrum of [Pd(Hmmtrz)₄]Cl₂ (**2**) in CDCl₃ exhibits signals at δ 3.58 and 7.91 ppm due to methyl and methine protons, respectively. In addition, the presence of a signal at δ

13.44 ppm due to N–H proton indicates that the ligand is bonded in the thione form in complex 2. The ¹³C NMR spectrum of [Pd $(Hmmtrz)_4$]Cl₂ (2) shows signals at δ 166.75, 140.93 and 31.53 ppm due to C=S, C=N (triazole ring) and CH_3 carbons, respectively. The ¹H NMR spectrum of the ligand 2-mercapto-5methyl-1,3,4-thiadiazole in DMSO-d₆ shows signals at 12.05, 3.32 and 2.49 ppm due to the thiadiazole NH. SH and methyl protons. respectively, indicating existence of the ligand in the thiol/thione tautomeric forms. The ¹H NMR spectrum of [Pd(Hmthd)₄]Cl₂ \cdot 2CHCl₃ (**3**) exhibits signals at δ 7.59 and 3.37 ppm for the CHCl₃ and CH₃ protons respectively, and a peak at δ 13.96 ppm for NH indicates the presence of thione form of the ligand in the complex. Appearance of a signal for NH in both the complexes suggests bonding of the neutral soft sulfur atom with the soft Pd(II) in complexes 2 and 3. The ¹³C NMR spectrum of [Pd(Hmthd)₄]Cl₂·2CHCl₃ (3) shows signals at δ 188.90 and 158.47 ppm due to C=S and C-N carbons, respectively.

3.4. Photoluminescence studies

In the present work, we have examined the photoluminescence properties of complexes **1**, **2** and **3** at room temperature and have tried to correlate them with the emission patterns of their respective free ligands. Complex $[Pd(eptu)_2]$ (**1**) shows photoluminescence at 25200 cm⁻¹ upon excitation at 31000 cm⁻¹. The free ligand, 3-mercapto-4-methyl-4H-1,2,4-triazole (Hmmtrz) displays photoluminescence at 18650 cm⁻¹ upon excitation at 29700 cm⁻¹ which has been ascribed as originating from intraligand π - π * transition [45]. Upon excitation of complex **2** at 38600 cm⁻¹, the corresponding emission was observed at 27000 cm⁻¹ (Figs. 1a and 1b) with a blue shift of 8350 cm⁻¹ as compared to the free ligand (Hmmtrz). Complexes [Cd(H₂trzS)₂Cl₂] and [Cd(H₂trzS)(H₂EDTA)] [27] exhibit blue shifts of 1300 and 600 cm⁻¹,



Fig. 1a. UV–Vis spectra of $[Pd(eptu)_2]$ (1), $[Pd(Hmmtrz)_4]Cl_2$ (2) and $[Pd(Hmthd)_4]$ $Cl_2\cdot 2CHCl_3$ (3).



Fig. 1b. Emission spectra of $[Pd(eptu)_2]$ (1), $[Pd(Hmmtrz)_4]Cl_2$ (2) and $[Pd(Hmthd)_4]Cl_2 \cdot 2CHCl_3$ (3) at the excitation wavelengths of 323, 259 and 310 nm for complexes 1, 2 and 3, respectively.

respectively as compared to the respective free ligand, which has been ascribed to the tautomerization of the triazole ring from thiol (in the free ligand) to the thione form in the above complexes which may increase the HOMO-LUMO energy gap. Similar phenomenon is also occurring in complex 2, because single crystal X-ray diffraction data of complex 2 supports thiol-thione tautomerization during complex formation. The free ligand, 2-mercapto-5-methyl-1,3,4-thiadiazole (Hmthd) is found to be an inferior fluorescent material in itself but it works as "turn-on" sensor upon complexation with Zn(II) [46]. Free Hmthd displays an emission at 22900 cm^{-1} upon excitation at 32600 cm^{-1} (Suppl. Figs. 1a and 1b). Photoluminescence studies indicate that complex [Pd(Hmthd)₄]Cl₂·2CHCl₃ (**3**) is a fluorescent material with a maximum emission at 26700 cm^{-1} with a blue shift of 3800 cm^{-1} as compared to the free ligand (Hmthd). The excitation spectra of complexes 1, 2 and 3 show maxima at 31800, 36000 and 32600 cm⁻¹ which are close to those observed in the absorption spectra (Fig. 1c).



Fig. 1c. Normalized excitation spectra of complexes 1, 2 and 3 at excitation wavelengths of 397, 370 and 375 nm, respectively.

3.5. Crystal structure description

The solid state structures of complexes **1–3** were determined by single crystal X-ray diffraction data. The details of data collection, structure solution and refinement are listed in Table 1. ORTEP diagram of complexes **1–3** with atom numbering schemes are shown in Figs. 2, 4 and 7, respectively. Selected bond lengths and angles are included in Tables 2–4. Hydrogen bonding parameters of complexes **2** and **3** are given in Tables 5 and 6, respectively.

3.5.1. Crystal structure description of $[Pd(eptu)_2](1)$

Fig. 2 shows ORTEP diagram of $[Pd(eptu)_2]$ (1) with atom numbering scheme. Palladium(II) centre in 1 forms two four membered PdNCS chelate rings using two monoanionic thiourea ligand utilizing thioamide sulfur and nitrogen atoms. In general, the ligand is expected to lose a proton from the thioamide nitrogen adjacent to the phenyl ring due to the resonance effect, and thus acts as a uninegative bidentate ligand. The carbon-sulfur (1.748 Å) and carbon-nitrogen (1.276 Å) distances within the chelate rings are comparable to the bond lengths in Heptu but longer than C=S and C=N double bonds, which suggest delocalization of the negative charge within the chelate ring and suggests coordination with sulfur and nitrogen atoms of the thiourea ligand [47]. The chelate and phenyl rings are tilted towards each other, making a dihedral angle of 34.30°. The Pd–S bond distances are found to be 2.337(3) and 2.345(3) Å for the two chelate rings, which are comparable to that reported for palladium thiourea complexes [Pd(tu)₄]I₂ (2.338 and 2.336 Å) [48] and *trans*-[Pd(PPh₃)₂(Dmtu)₂] Cl₂(H₂O)(CH₃OH)_{0.5} (2.323 and 2.336 Å) [49]. The Pd–N distances for the two chelate rings are 2.001(9) and 2.053(10) Å which are close to those reported for the palladium complex [PdL₂] $(ClO_4)_2 \cdot 2C_3H_6O$ (2.029 Å) [44]. The bond angles for N(3)-Pd(1)-S(1) (109.8(3)°), N(1)-Pd(1)-S(1) (70.1(2)°), N(3)-Pd(1)-S(2)(69.8(3)°) and N(1)-Pd(1)-S(2) (110.3(3)°) suggest a distorted square planar geometry around Pd(II) centre [50]. Molecular packing diagram of complex 1 shows that four complex molecules are present in one unit cell (Fig. 3).

3.5.2. Crystal structure description of $[Pd(Hmmtrz)_4]Cl_2(2)$

Fig. 4 shows ORTEP diagram of [Pd(Hmmtrz)₄]Cl₂ (**2**) with the atom numbering scheme. The ligand acts as monoanionic monodentate in complexes [Ag(mmtrz)₂(PPh₃)₂]·Hmmtrz and

Table 1		
Crystallographic data	for complexes	1, 2 and 3.

Parameters	1	2	3
Empirical formula	$C_{18}H_{22}N_4PdS_2$	$C_{12}H_{20}Cl_2N_{12}PdS_4$	$C_{14}H_{18}Cl_8N_8PdS_8$
Formula weight	464.94	637.94	944.84
Crystal system	monoclinic	triclinic	monoclinic
Space group	P 1 21/n 1	P1)	P 21/n
T (K)	293(2)	293(2)	293(2)
λ, Μο Κα (Å)	0.71073	0.71073	0.71073
a (Å)	10.3338(14)	8.2109(19)	8.750(5)
b (Å)	7.4314(11)	8.619(3)	11.648(5)
c (Å)	24.891(2)	9.915(2)	17.649(5)
α (°)	90.00	103.26(2)	90.00(5)
β (°)	89.95(10)	110.43(2)	104.05(5)
γ (°)	90.00	107.64(2)	90.00(5)
$V(Å^3)$	1911.5(4)	580.8(3)	1745.0(13)
Ζ	4	1	2
$\rho_{calcd} (g/cm^3)$	2.082	1.824	1.798
$\mu (\mathrm{mm}^{-1})$	2.250	1.417	1.647
F(000)	1172	320	936
Crystal size (mm ³)	$0.30\times0.28\times0.24$	$0.35 \times 0.25 \times 0.14$	$0.30 \times 0.27 \times 0.23$
θ range for data collections (°)	3.19–29.27	3.64-28.89	2.97-29.15
Index ranges	$-8 \leqslant h \leqslant 13, -10 \leqslant k \leqslant 8, -31 \leqslant l \leqslant 34$	$-10 \leqslant h \leqslant 10, -9 \leqslant k \leqslant 11, -13 \leqslant l \leqslant 7$	$-11 \leqslant h \leqslant 11, -9 \leqslant k \leqslant 15, -21 \leqslant l \leqslant 24$
No. of reflections collected	6197	4124	7501
No. of independent reflections (R_{int})	3606	2544	4688
No. of data/restrains/parameters	3606/0/226	2544/0/152	4688/0/173
Goodness-of-fit (GOF) on F ²	1.134	0.947	1.113
$R_1^{a}, wR_2^{b} [(I > 2\sigma(I))]$	0.0800, 0.2097	0.0424, 0.0791	0.0608, 0.1462
R_1^{a} , wR_2^{b} (all data)	0.1305, 0.2378	0.0698, 0.0894	0.0872, 0.1653
Largest difference in peak/hole (e Å ⁻³)	1.049, -0.983	0.823, -0.785	0.897, -0.811



Fig. 2. ORTEP diagram of [Pd(eptu)₂] (1) with atomic numbering scheme at 30% probability level.

Table 2
Interatomic distances (Å) and angles ($^{\circ}$) for complex [Pd(eptu) ₂] (1).

Bond length (Å)		Bond angles (°)		
Pd(1)-N(3)	2.001(9)	N(3)—Pd(1)—N(1)	178.9(4)	
Pd(1)-N(1)	2.053(10)	N(3) - Pd(1) - S(1)	109.8(3)	
Pd(1)-S(1)	2.337(3)	N(1) - Pd(1) - S(1)	70.1(2)	
Pd(1)-S(2)	2.345(3)	N(3) - Pd(1) - S(2)	69.8(3)	
S(1)-C(7)	1.727(10)	N(1) - Pd(1) - S(2)	110.3(3)	
S(2)—C(16)	1.749(11)	S(1) - Pd(1) - S(2)	177.81(14)	

Table 3 Interatomic distances (Å) and angles (°) for [Pd(Hmmtrz)₄]Cl₂ (**2**).

Bond length(Å)		Bond angles (°)	
Pd(1)—S(1A)	2.330(13)	S(1A)-Pd(1)-S(1A)	180.0
Pd(1)—S(1A)#1	2.330(13)	S(1A) - Pd(1) - S(1B)	93.43(4)
Pd(1)-S(1B)	2.341(11)	S(1A) - Pd(1) - S(1B)	86.57(4)
Pd(1)-S(1B)#1	2.341(11)	S(1A)-Pd(1)-S(1B) #1	86.57(4)
S(1A)-C(1A)	1.710(4)	S(1A)-Pd(1)-S(1B) #1	93.43(4)
S(1B)-C(1B)	1.696(4)	C(1A)— $S(1A)$ — $Pd(1)$	107.51(14
N(1B)-N(2B)	1.356(5)	C(1B)— $S(1B)$ — $Pd(1)$	104.31(12

Table 4	
Interatomic distances (Å) and angles (°) for $[Pd(Hmthd)_4]Cl)_2\cdot 2CHCl_3~(\textbf{3}).$	

Bond length (Å)		Bond angles (°)	
Pd(1)—S(2)	2.326(16)	S(2)—Pd(1)—S(2)	180.0(1)
Pd(1)-S(3)	2.331(2)	S(2) - Pd(1) - S(3)	88.38(6)
S(2) - C(3)	1.699(6)	S(2) - Pd(1) - S(3)	91.62(6)
S(4) - C(6)	1.721(6)	S(2) - Pd(1) - S(3)	91.62(6)
S(4) - C(5)	1.747(7)	S(2) - Pd(1) - S(3)	88.38(6)
S(1) - C(3)	1.728(6)	S(3) - Pd(1) - S(3)	180.0
S(1)-C(2)	1.743(6)	C(3) - S(2) - Pd(1)	107.3(2)

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 1, -z + 1.

 $[Hg(mmtrz)_2]_n$ while it behaves as a monoanionic monodentate as well as neutral bidentate in complex $[Hg_2(mmtrz)_4(Hmmtrz)_2]$ and connects two Hg(II) centres via its bridging behaviour [51]. In the crystallographic asymmetric unit of the complex [Pd(Hmmtrz)₄] Cl₂, the metal centre is coordinated with four neutral ligands using thione sulfur and two chlorides as counter ions. In complex 2, Pd (II) ion resides in a distorted square planar geometry with bond angles for S(1A)-Pd(1)-S(1B) (93.43(4)°) and S(1A)-Pd(1)-S(1B) #1 (86.57(4)°). The Pd(II) centre in 2 is bonded to sulfur atoms of four triazole molecules at the Pd(1)-S(1A) and Pd(1)-S(1B) distances of 2.330(13) and 2.341(11) Å respectively, that are comparable to similar Pd(II) complexes reported in the literature [52]. The exocyclic S(1A)–C(1A) and S(1B)–C(1B) {[1.710(4) and 1.696 (4) Å]} distances are also in agreement with that of typical carbon sulfur double-bonds (C=S) [53], indicating that the exocyclic C-S bond is of double bond character and ligand is present in the thione form. This is further supported by the longer N(1A)–C(1A) and N (1B)–C(1B) bond lengths [1.319(5) and 1.315(5) Å], than the N=C double bonds [1.27 Å] [54]. Two Pd(1)–S(1A) distances are

Table 5				
Weak intermolecular interactions	[Å and °	in	Pd(Hmmtrz) ₄ Cl ₂	(2).



Fig. 4. ORTEP diagram of $[Pd(Hmmtrz)_4]^{2+}$ cation of complex **2** with atomic numbering scheme at 30% probability level. Chlorine atoms are omitted for clarity.

shorter than other two Pd(1)—S(1B) which indicates that the former pair of sulfur atoms are strongly bonded with Pd(II) than the latter. In the solid state, complex **2** exhibits weak intermolecular C—H···N interactions between hydrogen of one triazole and nitrogen of the other triazole ring (Fig. 5) forming an extended network. The complex **2** is further stabilized by intramolecular N—H···Cl hydrogen bonding (Fig. 6).

D—H···A	d(D—H)	$d(H{\cdots}A)$	$d(D{\cdots}A)$	<(DHA)	Symmetry equivalent operators
N(1A) - H(1A) - Cl(1)#1	0.88(4)	2.15(5)	3.028(4)	175.0(5)	-x + 1, -y + 1, -z + 1
N(1B) - H(1B) - Cl(1)	0.75(4)	2.35(4)	3.088(4)	170.0(4)	x + 1, y + 1, z + 1

Table 6 Weak intermolecular interactions [Å and $^\circ]$ in $[Pd(Hmthd)_4]Cl)_2\cdot 2CHCl_3$ (3).

D—H····A	d(D—H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D\!\cdots\!A)$	<(DHA)	Symmetry equivalent operators
C(4)−H(4A)····S(1)	0.96(4)	2.95(5)	3.72(4)	138.0(5)	0.5 + x, 0.5 - y, -1 + z



Fig. 3. Molecular packing diagram of complex 1.



Fig. 5. C-H...N interaction in complex 2 leading to 1D structure.



Fig. 6. Packing diagram of complex 2 showing intramolecular N-H…Cl hydrogen bonding.

3.5.3. Crystal structure description of [Pd(Hmthd)₄]Cl₂·2CHCl₃ (**3**)

Fig. 7 shows ORTEP diagram of $[Pd(Hmthd)_4]Cl_2 \cdot 2CHCl_3$ (3) with the atom numbering scheme. In this complex, Pd(II) ion adopts a distorted square planar geometry with S(2)-Pd(1)-S(3) and S(2)-Pd(1)-S(3) bond angles of 91.62(6) and 88.38(6)°, respectively. The Pd(II) centre is bonded with four sulfur atoms of thiadiazole ring at the Pd(1)–S(2) and Pd(1)–S(3) distances of 2.326(16) and 2.331(2) Å, respectively. It is reported that the ligand behaves as monoanionic monodentate in its Cu(II), Hg(II), Cd(II) and Zn(II) complexes [46]. Interaction of ligand in the Cu(II) complex is ionic in nature, whereas it is covalently bonded through sulfur in its Cd (II) complex [46]. The ligand behaves as neutral monodentate in the complex $[Pd(Hmthd)_4]Cl_2 \cdot 2CHCl_3$ (3) and is bonded through the thione sulfur to the Pd(II) centre. The exocyclic S(2)-C(3)[1.699(6) Å] bond length is shorter than endocyclic S(1)–C(3) [1.728(6) Å] bond length, and is close to the carbon sulfur double-bonds (S=C), which indicates that the exocyclic sulfur has double bond character and the ligand is present in the thione form. This is further supported by the N(2)–C(3) bond length [1.320(8)] Å], which is longer than the N=C double bond [1.270 Å] [54]. The crystal structure of the complex revealed the presence of intermolecular N-H···Cl and C-H···Cl hydrogen bonding interactions between CH hydrogen of thiadiazole NH and methyl CH and chlorine atom present in the outer sphere of the complex (Fig. 8). The crystal structure is further supported by weak intermolecular C-H...S hydrogen bonding occurring between the CH hydrogen of methyl and sulfur atom of thiadiazole ring (Fig. 9).



Fig. 7. ORTEP diagram of $[Pd(Hmthd)_2]^{2+}$ cation of complex **3** with atomic numbering scheme at 30% probability level. Chlorine and chloroform are not shown for clarity.



Fig. 8. Showing intermolecular N-H···Cl, C-H···Cl and C-H···S hydrogen bonding leading to a linear chain structure in complex 3. Chlorine atoms are presented in ball and stick model.



Fig. 9. Showing intermolecular C-H···S hydrogen bonding leading to a cross-linked linear chain structure in complex 3.

To know the tautomeric form present in both the complexes, bond lengths within the triazole/thiadiazole ring were compared with the reported complexes. It is found that the carbon–sulfur and carbon–nitrogen bond lengths in the two polymorphic structures correspond to the thione form. In fact, the average carbon sulfur bond length of 1.696–1.710 Å for complex **2** and 1.698–1.747 Å for complex **3** are slightly longer than the carbon sulfur double bond whereas carbon–nitrogen distances of 1.319 and 1.284 Å for complex **2** and 1.324 and 1.289 for complex **3** are shorter than the single bond, indicating electron delocalization in the ring. The above results suggest that the neutral thione form of the ligand is bonded to the metal and there is extensive electron delocalization within the triazole/thiadiazole ring [55].

4. Conclusions

This paper reports on the syntheses, spectral and crystal structure investigations of three new Pd(II) complexes, $[Pd(eptu)_2]$ (1), $[Pd(Hmmtrz)_4]Cl_2$ (2) and $[Pd(Hmthd)_4]Cl_2 \cdot 2CHCl_3$ (3). The single crystal X-ray structures show four coordinate distorted square planar geometry around Pd(II) centre in these complexes. The thiourea ligand, Heptu is bonded to the metal ion through nitrogen and sulfur atoms and acts as a uninegative bidentate in complex **1**. The triazole (Hmmtrz) and thiadiazole (Hmthd) ligands act as neutral monodentate, coordinated to the metal ion through the thione sulfur in complexes **2** and **3**. The complexes are stabilized *via* intermolecular as well as intramolecular hydrogen bonding. Complexes **1**, **2** and **3** are fluorescent materials which upon excitation at 31000, 38600 and 32300 cm⁻¹ exhibit an emission at 25200, 27000 and 26700 cm⁻¹, respectively as a consequence of intraligand π - π * transitions.

Acknowledgements

P. Bharati thanks 'CSIR' – 'India' for the award of a SRF. Dr. N.K. Singh is thankful to 'UGC' – 'India' for the award of UGC-Emeritus Fellowship (2014-2015). Dr. M.K. Bharty is thankful to the 'Science and Engineering Research Board' – 'India' for the award of a Project (No. SERB/F/372/2015-16).

Appendix A. Supplementary material

CCDC 1403445, 1403446 and 1403447 contain the supplementary crystallographic data for complexes **1**. **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.01.003.

References

- [1] J. Cernak, J. Chomic, P. Kutschy, D. Svercinova, M. Dzurilla, Inorg. Chim. Acta 181 (1991) 85.
- [2] M.J. Moloto, M.A. Malik, P. O'Brien, M. Motevalli, G.A. Kolawole, Polyhedron 22 (2003) 595.
- [3] M. Lipowska, B.L. Hayes, L. Hansen, A. Taylor, L.G. Marzilli, Inorg. Chem. 35 (1996) 4227.
- [4] M. Dominguez, E. Antico, L. Beyer, A. Aguirre, S. Garcia-Granda, V. Salvado, Polyhedron 21 (2002) 1429.
- [5] M. Schuster, B. Kugler, K.H. König, Fresenius J. Anal. Chem. 338 (1990) 717.
- [6] K.H. König, M. Schuster, G. Schneeweis, B. Steinbrech, Anal. Chem. 319 (1984) 66.
- [7] G. Avsar, H. Arslan, H.-J. Haupt, N. Külcü, Turk. J. Chem. 27 (2003) 281.
- [8] H. Arsalan, N. Kuku, Transition Met. Chem. 28 (2003) 816.
- [9] W. Henderson, B.K. Nicholson, M.B. Dinger, R.L. Bennett, Inorg. Chim. Acta 338 (2002) 210.
- [10] S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama, Dalton Trans. (1990) 2105.
- [11] D.J. Che, X.L. Yao, G. Li, Y.H. Li, J. Chem. Soc., Dalton Trans. 11 (1998) 1853. [12] H. Park, J.F. Britten, U. Mueller, J.Y. Lee, J. Li, J.B. Parise, Chem. Mater. 19 (2007)
- 1302.
- [13] Q.G. Zhai, C.Z. Lu, X.-Y. Wu, S.R. Batten, Cryst. Growth Des. 7 (2007) 2332.
- [14] H. Park, G. Krigsfeld, J.B. Parise, Cryst. Growth Des. 7 (2007) 736. [15] B. Liu, X.-C. Zhang, Inorg. Chem. Commun. 11 (2008) 1162.
- [16] D. Schweinfurth, S. Demeshko, M.M. Khusniyarov, S. Dechert, V. Gurram, M.R. Buchmeiser, F. Meyer, B. Sarkar, Inorg. Chem. 51 (2012) 7592. [17] J.G. Haasnoot, Coord. Chem. Rev. 131 (2000) 200.
- [18] S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Müller, M.B. Cingi, M. Lanfranchi, A.M.M. Lanfredi, J. Ribas, Inorg. Chem. 39 (2000) 1859.
- [19] O.G. Shakirova, A.V. Virovets, D.Yu. Naumov, Yu.G. Shvedenkov, V.N. Elochina, L.G. Lavrenova, Inorg. Chem. Commun. 5 (2002) 690.
- [20] N. Wang, Y.-C. Feng, W. Shi, B. Zhao, P. Cheng, D.-Z. Liao, S.-P. Yan, CrystEngComm 14 (2012) 2769.
- [21] B.L. Sharma, S.K. Tandon, Pharmazie 39 (H-12) (1984) 858.
- [22] M. Du, X.-J. Zhao, J. Mol. Struct. 694 (2004) 235.
- [23] F.A. Ashour, N.S. Habbib, Farmaco 45 (1990) 1341.
- [24] A. Foroumadi, M. Mirzaei, A. Shafiee, Pharmazie 56 (2001) 610.

- [25] Y. Nakagawa, K. Nishimura, K. Izumi, K. Kinoshita, T. Kimura, N. Kurihara, I. Pestic, Sci. 21 (1996) 195
- [26] Y.G. Wang, L. Cao, J. Yan, W.F. Ye, Q.C. Zhou, B.X. Lu, Chem. J. Chin. Univ. 20 (1999) 1903
- [27] R.B. Zhang, Z.J. Li, J.K. Cheng, Y.Y. Qin, J. Zhang, Y.G. Yao, Cryst. Growth Des. 8 (2008) 2562.
- [28] M.R. Gajendragad, U. Agarwala, Bull. Chem. Soc. Jpn. 48 (1975) 1024.
- [29] J. Tsuji, Palladium Reagents and Catalysts, Wiley, New York, 2004. Chapter 3.
- [30] F. Diederich, P.J. Stang, Metal-Catalyzed Cross-Coupling Reactions, VCH, Weinheim, 1997.
- [31] M. Beller, Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals, VCH, Weinheim, 2004.
- [32] A.M. Trzeciak, J.J. Ziołkowski, Coord. Chem. Rev. 251 (2007) 1281.
- [33] U. Christmann, R. Vilar, Angew. Chem., Int. Ed. 44 (2005) 366.
- [34] E. Dez-Barra, J. Guerra, V. Hornillos, S. Merino, J. Tejeda, Organometallics 22 (2003) 4610.
- [35] L.-Y. Wu, X.-Q. Hao, Y.-X. Xu, M.-Q. Jia, Y.-N. Wang, J.-F. Gong, M.-P. Song, Organometallics 28 (2009) 3369.
- [36] H. Wang, J. Liu, Y. Deng, T. Min, G. Yu, X. Wu, Z. Yang, A. Lei, Chem. Eur. J. 15 (2009) 1499
- [37] A. Singh, M.K. Bharty, P. Bharati, A. Bharti, S. Singh, N.K. Singh, Polyhedron 85 (2015) 918.
- [38] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.
- [39] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Crystallogr. 41 (2008) 466.
- [40] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849.
- [41] Y. Kawada, Y. Kataoka, Y. Ura, Dalton Trans. 42 (2013) 14844.
- [42] T. Kawamoto, I. Nagasawa, H. Kuma, Y. Kushi, Inorg. Chem. 35 (1996) 2427.
- [43] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, 1984.
- [44] V.V. Bon, S.I. Orysyk, V.I. Pekhnyo, V.V. Orysyk, S.V. Volkov, Polyhedron 26 (2007) 2935.
- [45] Y.-L. Wang, N. Zhang, Cryst. Growth Des. 11 (2011) 130.
- [46] P. Bharati, A. Bharti, M.K. Bharty, S. Kashyap, U.P. Singh, N.K. Singh, Polyhedron
- 63 (2013) 222. [47] J.R. Dilworth, J. Hyde, P. Lyford, P. Vella, K. Venkatasubramaman, J.A. Zubieta, Inorg. Chem. 18 (1979) 268.
- [48] G. De Munno, B. Gabriele, G. Salerno, Inorg. Chim. Acta 234 (1995) 181.
- [49] S. Nadeem, M. Bolte, S. Ahmad, T. Fazeelat, S.A. Tirmizi, M.K. Rauf, S.A. Sattar, S. Siddiq, A. Hameed, S.Z. Haider, Inorg. Chim. Acta 363 (2010) 3261.
- [50] M. Trivedi, G. Singh, R. Nagarajan, N.P. Rath, Inorg. Chim. Acta 394 (2013) 107.
- [51] A. Bharti, P. Bharati, M.K. Bharty, R.K. Dani, Polyhedron 54 (2013) 131.
- [52] L. Canovese, F. Visentin, P. Uguagliati, G. Chessa, A. Pesce, J. Organomet. Chem. 566 (1998) 61.
- [53] L.E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 18, The Chemical Society, London (1965).
- [54] X.Z. You, Progress in Coordination Chemistry, Higher Education Publishing Company, Beijing, 2000.
- [55] A. Carletta, C. Meinguet, J. Wouters, A. Tilborg, Cryst. Growth Des. 15 (2015) 2461.