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Dimeric cyclopalladated azobenzenes: structural differences between 2-hydroxypyridine and 2-mercaptopyridine bridged complexes

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Abstract

Binuclear chloro-bridged cyclopalladated azobenzenes $[Pd(A)Cl]_2$ (A = *ortho*-metallated azobenzene or its derivatives) have been reacted with aqueous (aq.) $AgNO_3$ followed by the addition of 2-hydroxypyridine (2-PyOH; donor centres of deprotonated form abbreviated N,O)/2-mercaptopyridine (2-PySH; donor centres of deprotonated form abbreviated N,S) in presence of Et_3N to synthesise bridged dinuclear compound $[Pd(A)(\mu\text{-}N,O)]_2$–$[Pd(A)(\mu\text{-}N,S)]_2$. The compositions of the complexes have been established by elemental analyses, IR, UV–vis, ^1H and ^{13}C-NMR spectral data. The structural confirmation has been carried out by X-ray crystallography. The structures show anti-symmetric metallacycle in the dimer and N,O/N,S bridging arrangement. The dimer $[Pd(A_1)(\mu\text{-}N,X)]_2$ shows strong Pd···Pd interaction (A_1 = 2-(phenylazo)benzene). The coordination mode in $[Pd(A_1)(\mu\text{-}N,O)]_2$ shows *trans* pyridine-N to Pd–N(azo) bond while in $[Pd(A_1)(\mu\text{-}N,S)]_2$ pyridine-N is *trans* to the Pd–C bond. The square planes are convergent towards heterocyclic bridging side. © 2002 Published by Elsevier Science B.V.

Keywords: Cyclopalladated azobenzenes; 2-Hydroxypyridine; 2-Mercaptopyridine; Bridged binuclear; X-ray structure; Electrochemistry

1. Introduction

Azobenzenes are C, N donor ligands and are good candidates to synthesise cyclometallated compounds of transition [1–19] and non-transition metals [20,21]. A majority of the reaction has been reported with palladium(II) [1–16]. Many reviews concerning their syntheses and reactivities appear in literature [1,11]. Cyclopalladated compounds have found numerous applications in organic syntheses [9–11], material science [12], biology [13] and metallomesogenic field [14]. Azobenzenes yield chloro/acetato bridged dinuclear cyclopalladated compounds [1,2] upon reaction with $[PdCl_4]^{2-}$ or $Pd(OAc)_2$, respectively. Acetato bridged cyclopalladated dimers exist in a folded anti-symmetric form with C_2-symmetry [3]. The bridge splitting reactions of the dimer with neutral and anionic ligands give mixed cyclopalladated complexes [5–8]. For example, the reaction [7] of $[Pd(A)Cl]_2$ with monoanionic N,O and S,S-chelators (A = azobenzenes; N,O = 8-quinolinolato, 2-picolinato, 2-quinaldato); (S,S = dithiocarbamate, xanthate) gives monocyclopalladated mixed complex [Pd(A)(N,O)]–[Pd(A)](S,S)] [7]. In the present paper we report, further new type of mixed dinuclear cyclopalladeted complexes of azobenzenes with 2-hydroxypyridine–2-mercaptopyridine having Pd···Pd interaction. 2-Hydroxypyridine (2-PyOH) and 2-mercaptopyridine (2-PySH) are versatile monoanionic bridging agent and forms large number of complexes with unusual M···M interaction in platinum metal chemistry [22–26]. Donor centres are abbreviated in deprotonated, 2-PyOH as N, O and in deprotonated, 2-PySH as N,S. Bridged dimer $[Pd(A)(\mu\text{-}N,O)]_2$ exhibits stronger Pd···Pd interaction than $[Pd(A)(\mu\text{-}N,S)]_2$. The binding mode and atom numbering pattern is shown in Scheme 1. The coordination mode in $[Pd(A)(\mu\text{-}N,O)]_2$ exhibits *trans* pyridine-N to Pd–N(azo) bond while in $[Pd(A)(\mu\text{-}N,S)]_2$ pyridine-N is *trans* to the Pd–C bond. Single crystal X-

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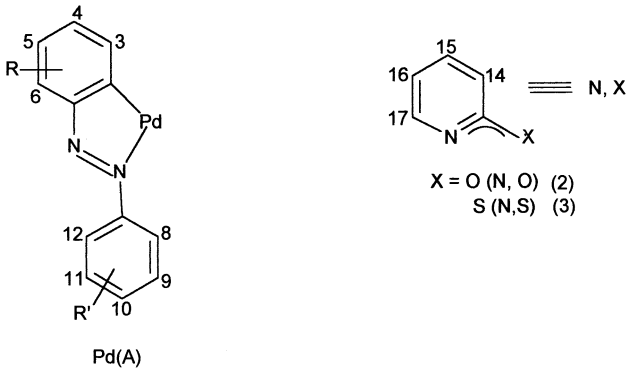

Scheme 1. A_1: R = R′ = H (**1a/2a/3a**); A_2: R = 4-Me, R′ = H (**1b/2b/3b**); A_3: R = H, R′ = 10-Me (**1b′/2b′/3b′**); A_4: R = 4-Me, R′ = 10-Me (**1c/2c/3c**); A_5: R = R′ = 4-Cl (**1d/2d/3d**).

ray structure studies of the complexes confirm their structural differences.

2. Experimental

2-Hydroxypyridine was obtained from Aldrich and used as received. Palladium chloride was received from Arora Matthey, Calcutta, India. Azobenzenes and chlorobridged cyclopalladated azobenzenes were synthesised as reported earlier [7]. Dichloromethane, chloroform and acetonitrile for spectroscopic and electrochemical work were purified and dried by known procedures [18]. All other chemicals and solvents were reagent grade and were used as received.

IR spectra (KBr disk) were recorded on JASCO model 420 FT-IR spectrophotometer. UV–vis spectra were obtained using JASCO UV–vis–NIR model V-570 spectrophotometer. ^{1}H and $^{13}C\{^1H\}$-NMR spectra were collected from Bruker 300 MHz FT-NMR spectrometer in $CDCl_3$ using tetramethylsilane as internal reference. Elemental analyses were performed using Perkin–Elmer 2400 CHN elemental analyser.

2.1. Preparation of complexes

2.1.1. *[Pd(A$_1$)(μ-N,O)]$_2$ (**2a**)*

To an acetone solution (15 ml) of $[Pd(A_1)Cl]_2$ (0.2 g, 0.31 mM) was added aq. $AgNO_3$ (0.11 g, 0.65 mM) solution. The mixture was refluxed for 2 h. The precipitated AgCl was filtered at hot condition through G-4 sintered crucible. To this orange solution 2-hydroxypyridine in acetone solution (10 ml) in presence of Et_3N (0.06 g, 0.63 mM) was added dropwise with continuous stirring (1 h) under nitrogen atmosphere. The colour of the solution turned to brown–red and the precipitate appeared slowly on bubbling nitrogen gas. The precipitate was filtered, washed with water, and crystallised from chloroform–hexane via diffusion. The product was dried over $CaCl_2$, yield, 0.165 g, 70%. Anal. Found: C, 53.40; H, 3.30; N, 11.09. $C_{34}H_{26}N_6O_2Pd_2$ (**2a**) Calc.: C, 53.49; H, 3.41; N, 11.01%. ^{1}H-NMR ($CDCl_3$): 6.05 (d, 1H, H(3), $^3J_{HH} = 7.5$ Hz), 6.55 (t, 1H, H(4), $^3J_{HH} = 7.0$ Hz), 6.90 (t, 1H, H(5), $^3J_{HH} = 7.5$ Hz), 7.04 (m, 2H, H(10,14)), 7.22 (t, 2H, H(15,16), $^3J_{HH} = 7.5$ Hz), 7.71 (d, 1H, H(6), $^3J_{HH} = 9.0$ Hz), 7.74 (d, 2H, H(8,12), $^3J_{HH} = 6.9$ Hz), 8.00 (d, 1H, H(17), $^3J_{HH} = 7.0$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): four pairs of quaternary C-centres at 170.443, 161.266, 148.541, 142.546; 13 pairs of CH centres at 148.582, 137.625, 134.910, 129.687, 128.291, 128.291, 127.637, 127.637, 130.343, 123.708, 117.496 and 110.536.

2.1.2. *[Pd(A$_2$/A$_3$)(μ-N,O)]$_2$ (**2b/2b′**)*

The reaction between $[Pd(A_2/A_3)Cl]_2$ (**1b/1b′**) (0.2 g, 0.30 mM) and 2-PyOH (0.06g, 0.63 mM) as before has synthesised $[Pd(A_2/A_3)(\mu\text{-N,O})]_2$ (**2b/2b′**) and isolated in 75% yield. Anal. Found: C, 54.55; H, 3.70; N, 10.50. $C_{36}H_{30}N_6O_2Pd_2$ (**2b/2b′**). Calc.: C, 54.63; H, 3.79; N, 10.60%. ^{1}H-NMR ($CDCl_3$) spectra give complicated spectral pattern in the range 6.0–8.0 ppm, which may be due to isomer mixing and have not been assigned.

2.1.3. *[Pd(A$_4$)(μ-N,O)]$_2$ (**2c**)*

The reaction between $[Pd(A_4)Cl]_2$ (0.2 g, 0.28 mM) and 2-PyOH (0.06 g, 0.63 mM) as before has synthesised $[Pd(A_4)(\mu\text{-N,O})]_2$ (**2c**) and isolated in 68% yield. Anal. Found:. C, 55.60; H, 4.10; N, 10.20. $C_{38}H_{34}N_6O_2Pd_2$ (**2c**). Calc.: C, 55.69; H, 4.15; N, 10.25% ^{1}H-NMR ($CDCl_3$): 5.75 (s, 1H, H(3)), 6.84 (d, 1H, H(5), $^3J_{HH} =$ 6.9 Hz), 6.88 (d, 2H, H(9,11), $^3J_{HH} = 9.0$ Hz), 6.95 (d,1H, H(14), $^3J_{HH} = 8.1$ Hz), 7.23 (t, 2H, H(15,16), $^3J_{HH} = 6.9$ Hz), 7.55 (d, 1H, H(6), $^3J_{HH} = 8.1$ Hz), 7.60 (d, 2H, H(8,12), $^3J_{HH} = 8.1$ Hz), 8.03 (d, 1H, H(17), $^3J_{HH} = 6.9$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): six pairs of quaternary C-centres at 170.348, 161.266, 156.212, 149.589, 141.969, 129.415; 11 pairs of CH centres at 148.198, 137.579, 134.875, 128.673, 128.363, 128.363, 126.242, 123.579, 123.579, 117.476 and 110.460. -Me signals at 22.295 and 21.309 ppm.

2.1.4. *[Pd(A$_5$)(μ-N,O)]$_2$ (**2d**)*

The reaction between $[Pd(A_5)Cl]_2$ (0.2 g, 0.26 mM) and 2-PyOH (0.06 g, 0.63 mM) as before has synthesised $[Pd(A_5)(\mu\text{-N,O})]_2$ (**2d**) and isolated in 72% yield. Anal. Found: C, 45.20; H, 2.40; N, 9.25. $C_{34}H_{22}N_6O_2Cl_4Pd_2$ (**2d**). Calc.: C, 45.29; H, 2.44; N, 9.32%.^{1}H-NMR ($CDCl_3$): 5.88 (s, 1H, H(3)), 6.96 (d, 1H, H(5), $^3J_{HH} =$ 6.9 Hz), 7.05 (d, 1H, H(14), $^3J_{HH} = 8.1$ Hz), 7.14 (d, 2H, H(9,11), $^3J_{HH} = 6.9$ Hz), 7.28 (t, 2H, H(15,16), $^3J_{HH} =$ 6.9 Hz), 7.60 (d, 1H, H(6), $^3J_{HH} = 8.1$ Hz), 7.72 (d, 2H, H(8,12), $^3J_{HH} = 8.1$ Hz), 7.96 (d, 1H, H(17), $^3J_{HH} = 6.9$ Hz). The compound is not sufficiently soluble to run $^{13}C\{^1H\}$-NMR ($CDCl_3$) spectrum.

*2.1.5. [Pd(A1)(μ-N,S)]2 (**3a**)*

The reaction between $[Pd(A_1)Cl]_2$ (**1a**) (0.2 g, 0.29 mM) and 2-PySH (0.06g, 0.54 mM) as before has synthesised $[Pd(A_1)(\mu\text{-N,S})]_2$ (**3a**) and isolated in 67% yield. Anal. Found: C, 51.50; H, 3.07; N, 10.50. $C_{34}H_{26}N_6S_2Pd_2$ (**3a**). Calc.: C, 51.33; H, 3.27; N, 10.57%. ^{1}H-NMR ($CDCl_3$): 6.08 (d, 1H, H(3), $^3J_{HH}$ = 7.5 Hz), 6.56 (t, 1H, H(4), $^3J_{HH} = 9.0$ Hz), 6.88 (t, 1H, H(5), $^3J_{HH} = 9.0$ Hz), 7.00 (d,1H, H(14), $^3J_{HH} = 7.5$ Hz), 7.06 (t, 2H, H(9,11), $^3J_{HH} = 7.5$ Hz), 7.03 (t, 1H, H(10), $^3J_{HH} = 9.0$ Hz), 7.20 (t, 2H, H(15,16), $^3J_{HH} = 9.0$ Hz), 7.37 (d, 2H, H(8,12), $^3J_{HH} = 9.0$ Hz), 7.60 (d, 1H, H(6), $^3J_{HH} = 7.5$ Hz), 8.36 (d, 1H, H(17), $^3J_{HH} = 6.0$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): four pairs of quaternary C-centres at 168.541, 156.283, 147.081, 131.846; 13 pairs of CH centres at 145.192, 133.618, 132.841, 130.140, 128.840, 128.840, 126.038, 126.038, 129.378, 117.789, 114.548, 103.889 and 110.460.

*2.1.6. [Pd(A2/A3)(μ-N,S)]2 (**3b/3b′**)*

The reaction between $[Pd(A_2/A_3)Cl]_2$ (**1b/1b′**) (0.2 g, 0.30 mM) and 2-PySH (0.06 g, 0.54 mM) as before has synthesised $[Pd(A_2/A_3)(\mu\text{-N,S})]_2$ (**3b/3b′**) and isolated in 70% yield. Anal. Found: C, 52.38; H, 3.57; N, 10.30. $C_{36}H_{30}N_6S_2Pd_2$ (**3b/3b′**). Calc.: C, 52.50; H, 3.65; N, 10.21%. ^{1}H-NMR ($CDCl_3$) spectra give complicated spectral pattern in the range 6.0–8.0 ppm, which may be due to isomer mixing and have not been assigned.

*2.1.7. [Pd(A4)(μ-N,S)]2 (**3c**)*

The reaction between $[Pd(A_4)Cl]_2$ (**1c**) (0.2 g, 0.28 mM) and 2-PySH (0.06g, 0.54 mM) as before has synthesised $[Pd(A_4)(\mu\text{-N,S})]_2$ (**3c**) and isolated in 72% yield. Anal. Found: C, 53.48; H, 3.87; N, 9.72. $C_{38}H_{34}N_6S_2Pd_2$ (**3c**). Calc.: C, 53.60; H, 4.00; N, 9.87%. ^{1}H-NMR ($CDCl_3$): 5.85 (s, 1H, H(3)), 6.83 (m, 3H, H(5,9,11), 7.02 (d, 1H, H(14), $^3J_{HH} = 7.5$ Hz), 7.15 (t, 2H, H(15,16), $^3J_{HH} = 9.0$ Hz), 7.25 (d, 2H, H(8, 12), $^3J_{HH} = 9.0$ Hz), 7.55 (d, 1H, H(6), $^3J_{HH} = 7.5$ Hz), 8.30 (d, 1H, H(17), $^3J_{HH} = 6.0$ Hz). $^{13}C\{^1H\}$-NMR ($CDCl_3$): six pairs of quaternary C-centres at 169.045, 158.830, 154.742, 146.521, 138.019, 125.518; 11 pairs of CH centres at 144.849, 136.059, 133.521, 127.849, 125.591, 125.591, 121.432, 121.432, 120.492, 113.678, 104.077. -Me signals at 20.843 and 19.789 ppm.

*2.1.8. [Pd(A5)(μ-N,S)]2 (**3d**)*

The reaction between $[Pd(A_5)Cl]_2$ (**1d**) (0.2 g, 0.26 mM) and 2-PySH (0.06g, 0.54 mM) as before has synthesised $[Pd(A_5)(\mu\text{-N,S})]_2$ (**3d**) and isolated in 75% yield. Anal. Found: C, 43.58; H, 2.27; N, 9.12. $C_{34}H_{22}N_6S_2Pd_2$ (**3d**). Calc.: C, 43.74; H, 2.36; N, 9.01%. ^{1}H-NMR ($CDCl_3$): 6.13 (s, 1H, H(3)), 6.91 (d, 1H, H(5), $^3J_{HH} = 9.0$ Hz), 7.06 (d, 1H, H(14), $^3J_{HH} = 7.5$ Hz), 7.27 (m, 2H, H(15,16)), 7.30 (d, 2H, H(9,11), $^3J_{HH} = 7.5$ Hz), 7.42 (d, 2H, H(8,12), $^3J_{HH} = 9.0$ Hz), 7.63 (d, 1H, H(6), $^3J_{HH} = 7.5$ Hz), 8.41 (d, 1H, H(17), $^3J_{HH} = 6.0$ Hz). The compound is not sufficiently soluble to run $^{13}C\{^1H\}$-NMR ($CDCl_3$) spectrum.

2.2. X-ray diffraction studies

Crystal suitable for X-ray work was grown by slow diffusion of dichloromethane solution into hexane at 298 K. The crystal size are $0.20 \times 0.14 \times 0.11$ and $0.55 \times 0.40 \times 0.08$ mm^3 for **2a** and **3a**, respectively. X-Ray diffraction data was collected at 295(2) K with the Siemens SMART CCD using graphite-monochromatised Mo–K_α radiation ($\lambda = 0.71073$ Å). A summary of the crystallography data and structure refinement parameters are given in Table 1. The collected reflections were 6478 and 38 879 for **2a** and **3a**, respectively. Of them, the reflections recorded using ω-scan technique were 5491 for **2a** and 7763 for **3a**. Intensities were corrected for Lorentz and polarisation factors. Semi-empirical corrections based on ψ-scan were applied. The structure was solved by heavy atom methods using SHELXS-97 and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using riding model. In the final difference Fourier map the residual maxima and minima were 0.295 and 0.640 e Å^{-3} for **2a** and 0.480 and −0.891 e Å^{-3}. All calculations were carried out using the SHELX-97.

Table 1
Summarised crystallographic data for $[Pd(A_1)(N,X)]_2$

Crystal parameters	**2a**	**3a**
Empirical formula	$C_{34}H_{26}N_6O_2Pd_2$	$C_{34}H_{26}N_6S_2Pd$
Formula weight	763.41	795.53
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a (Å)	10.3900(6)	17.949(7)
b (Å)	14.1283(8)	16.084(7)
c (Å)	20.3941(12)	22.181(7)
β (°)	90.619(1)	90
V (Å^3)	2993.5(3)	6403(4)
Z	4	8
D_{calc} (g cm^{-3})	1.694	1.650
μ (Mo–K_α) (cm^{-1})	12.44	12.88
2θ max (°)	55	55
Number of unique reflections	6478	38 879
Number of observed data ($I > 2\sigma(I)$)	5491	7763
Parameters refined	398	397
R	0.0227	0.050
R_w	0.0545	0.0977
Goodness-of-fit	1.058	1.041

3. Results and discussion

3.1. Synthesis

Binuclear chloro-bridged cyclopalladeted azobenzenes $[Pd(A)Cl]_2$ used as starting compound for the synthesis of the compounds in the present report. Treatment of $[Pd(A)Cl]_2$ in CH_2Cl_2 solution with 2-hydroxypyridine (deprotonated form is abbreviated N,O)/2-mercaptopyridine (deprotonated form is abbreviated N,S) in the presence of sodium methoxide (NaOMe) give a new product in the yield of 20–30%. The reaction of $[Pd(A)Cl]_2$ with $AgNO_3$ (aq.) in boiling acetone solution and the subsequent treatment of 2-hydroxypyridine–2-mercaptopyridine in presence of Et_3N synthesised the same product in 65–70% yield. The second method has been used for the synthesis of the complexes. The complexes were characterised by microanalyses, IR, ^1H, and ^{13}C-NMR spectral data. The complexes are fairly soluble in organic solvents and non-conducting in nature. The azobenzenes and the products obtained are shown in Scheme 1.

$$\underset{\mathbf{1}}{[Pd(A)Cl]_2} + N,X \overset{(i)\ or}{\underset{(ii)}{\rightarrow}} \underset{\mathbf{2/3}}{[Pd(A)(\mu - N,X)]_2}$$

(i) 2-Hydroxypyridine (2-PyOH)–2-mercaptopyridine (2-PySH) in CH_2Cl_2 + NaOMe; (ii) $AgNO_3$ (aq.) solution in acetone + 2-PyOH–2-PySH in presence of Et_3N.

3.2. X-Ray structure study

The X-ray structure of $[Pd(A_1)(\mu\text{-}N,O)]_2$ (**2a**) and $[Pd(A_1)(\mu\text{-}N,S)]_2$ (**3a**) have been determined. Perspective molecular views are shown in Figs. 1 and 2 and the selected bond parameters are listed in Table 2.

3.2.1. Geometrical features

Azobenzene binds as bidentate chelating C,N-fashion about palladium(II) and 2-pyridone (μ-N,O)–2-mercaptopyridone (μ-N,S) act as bidentate bridging ligand.

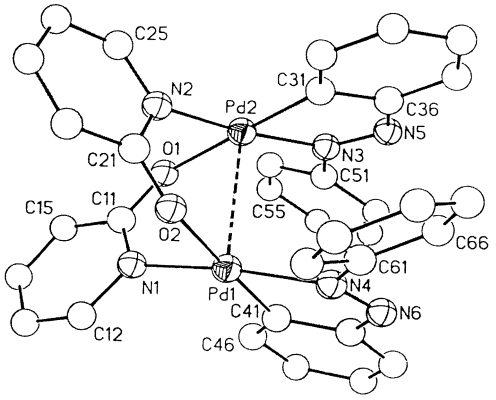

Fig. 1. Single crystal X-ray structure of $[Pd(A_1)(\mu\text{-}N,O)]_2$ (**2a**).

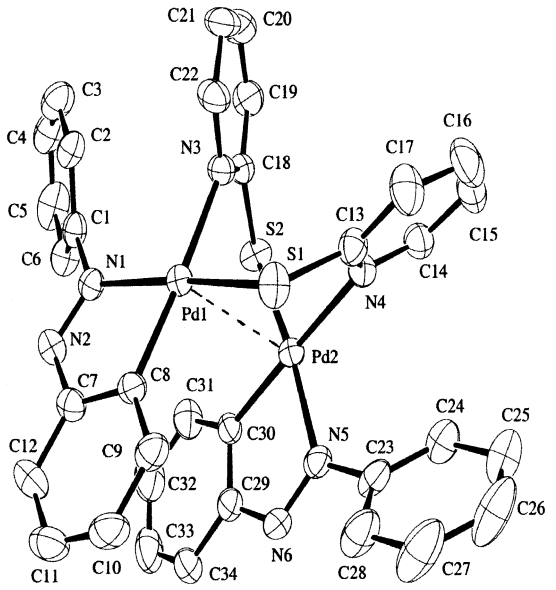

Fig. 2. Single crystal X-ray structure of $[Pd(A_1)(\mu\text{-}N,S)]_2$ (**3a**).

Table 2
Selected bond lengths and angles

Distance (Å)		Angle (°)	
$[Pd(A_1)(\mu\text{-}N,O)]_2$ (**2a**)			
Pd(1)–C(41)	1.955(2)	C(41)–Pd(1)–N(4)	79.21(9)
Pd(1)–N(4)	2.037(2)	N(1)–Pd(1)–O(2)	88.57(7)
Pd(1)–N(1)	2.042(2)	N(1)–Pd(1)–N(4)	171.70(8)
Pd(1)–O(2)	2.113(16)	C(41)–Pd(1)–O(2)	178.34(8)
Pd(2)–C(31)	1.959(2)	C(31)–Pd(2)–N(3)	94.28(8)
Pd(2)–N(3)	2.043(2)	N(2)–Pd(2)–O(1)	87.26(7)
Pd(2)–N(2)	2.043(2)	N(2)–Pd(2)–N(3)	173.23(7)
Pd(2)–O(1)	2.111(2)	C(31)–Pd(2)–O(1)	178.46(8)
N(4)–N(6)	1.268(3)		
N(3)–N(5)	1.276(2)		
Pd(1)···Pd(2)	2.840(3)		
$[Pd(A_1)(\mu\text{-}N,S)]_2$ (**3a**)			
Pd(1)–C(8)	1.981(4)	N(1)–Pd(1)–C(8)	78.7(2)
Pd(1)–N(1)	2.067(4)	N(3)–Pd(1)–S(1)	91.3(1)
Pd(1)–N(3)	2.119(4)	N(1)–Pd(1)–S(1)	171.2(1)
Pd(1)–S(1)	2.299(1)	C(8)–Pd(1)–N(3)	174.6(2)
Pd(2)–C(30)	1.965(4)	N(4)–Pd(2)–S(2)	91.1(1)
Pd(2)–S(2)	2.298(1)	C(30)–Pd(2)–N(4)	176.6(2)
N(1)–N(2)	1.272(5)	N(5)–Pd(2)–S(2)	170.0(1)
N(5)–N(6)	1.274(5)	N(5)–Pd(2)–C(30)	78.4(2)
Pd(1)···Pd(2)	2.878(1)		

Molecular unit consists of a C,N-cyclopalladated dimer in a folded arrangement with C_2-symmetry bridged by N,O/N,S group. The chelate ring, Pd(C,N), is planar (deviation < 0.03 Å) and the chelate angle, C–Pd–N, lies 79.3 ± 0.1° in $[Pd(A_1)(\mu\text{-}N,O)]_2$ (**2a**) and 78.5 ± 0.2° in $[Pd(A_1)(\mu\text{-}N,S)]_2$ (**3a**). The pendant phenyl ring to cyclopalladated fragment is no longer planar with the chelate fragment. It is twisted by av. 35 and 45° from the Pd(C,N) plane for **2a** and **3a**, respectively. In $[Pd(A_1)(\mu\text{-}N,O)]_2$ (**2a**) the atomic arrangements N(1), C(41), N(4),

O(2), Pd(1) and N(2), C(31), N(3), O(1), Pd(2) constitute two independent square planes (deviation < 0.05 Å). In $[Pd(A_1)(\mu\text{-N,S})]_2$ (**3a**) the square planes are N(1), C(8), N(3), S(1), Pd(1) and N(5), C(30), N(4), S(2), Pd(2) are planar with mean deviation is < 0.05 Å. These two square planes in **2a/3a** are convergent towards heterocyclic-binding site. Viewed down the Pd···Pd axis projects the molecule in a distorted 'gauche' conformation (Fig. 3) with following interplanar angles:

O(1)–Pd(2)···Pd(1)–N(1)	17.45°	S(2)–Pd(2)···Pd(1)–N(3)	38.44°
O(2)–Pd(1)···Pd(2)–N(2)	18.89°	S(1)–Pd(1)···Pd(2)–N(4)	38.84°
C(31)–Pd(2)···Pd(1)–N(4)	23.17°	C(8)–Pd(1)···Pd(2)–N(5)	34.27°
C(41)–Pd(1)···Pd(2)–N(3)	23.16°	C(30)–Pd(2)···Pd(1)–N(1)	35.14°

Angular deviation is higher in $[Pd(A_1)(\mu\text{-N,S})]_2$ (**3a**) than that of $[Pd(A_1)(\mu\text{-N,O})]_2$ (**2a**) and may be due to larger strain provided by thiolato-S in **3a** compared with phenolato-O in **2a**. This strain is originated undoubtedly from bulkier size of S than O. The angles extended by N–Pd–S in **3a** is contracted by $> 2°$ compared with that of N–Pd–O in **2a** which may be due to larger atomic size of coordinated-S (μ-N,S) than that of coordinated-O (μ-N,O). *Trans* angles are deviated from linearity and may be due to angular strain provided by cyclopalladated ring.

3.2.2. Bond parameters

The Pd–C bond lengths are av. 1.96 Å in **2a** and 1.97 Å in **3a**. There are two types of Pd–N bonds: Pd–N(py) and Pd–N(azo). In $[Pd(A_1)(\mu\text{-N,O})]_2$ (**2a**) the Pd–N distances are closely spaced: Pd–N(py): Pd(1)–N(1), 2.042(2); Pd(2)–N(2), 2.043(2) and Pd–N(azo): Pd(1)–N(4), 2.037(2); Pd(2)–N(3), 2.043(2) Å. In $[Pd(A_1)(\mu\text{-N,S})]_2$ (**3a**) the Pd–N(py) bond lengths are Pd(1)–N(3), 2.119(4); Pd(2)–N(4), 2.129(4) Å and they are longer than Pd–N(azo) bond lengths: Pd(1)–N(1), 2.067(4); Pd(2)–N(5), 2.082(4) Å. Elongation of Pd–N(py) bond distances in $[Pd(A_1)(\mu\text{-N,S})]_2$ (**3a**) compared with $[Pd(A_1)(\mu\text{-N,O})]_2$ (**2a**) by > 0.08 Å and that may be due to strong *trans* influence of the Pd–C bond in former whereas in $[Pd(A_1)(\mu\text{-N,O})]_2$ (**2a**) the Pd–C bond is *trans* to Pd–O bond. The Pd–O and Pd–S distances are found to be longest in **2a** and **3a**, respectively. The N=N distance is av. 1.27 Å and slightly elongated than free ligand values (1.25 Å) [27]. This is an indication of metal–ligand π-interaction localised in the M-azo fragment [28].

It is observed that O(μ-N,O) prefers to bind Pd(II) *trans* to the Pd–C bond in **2a** while pyridine-N(μ-N,S) is bonded *trans* to the Pd–C bond in **3a**. The Pd···Pd axis is not directly perpendicular to the square planes and the deviation supports convergence of the square planes towards heterocyclic bridging unit. In **2a**, the interatomic contacts of 2-pyridone, N(1)···O(1) (2.295 Å)/N(2)···O(2) (2.298 Å) are shorter than distances of azobenzene fragment of Pd(C,N) unit, C(31)···C(41) (4.681 Å)/N(4)···N(3) (4.079 Å). Similarly in **3a** the contacts of 2-mercaptopyridone, N(4)···S(1) (2.690 Å)/N(3)···S(2) (2.695 Å) are shorter than distances in cyclopalladaed unit, C(8)···C(30) (3.606 Å)/N(1)···N(5) (5.153 Å). The conformation of the bridged square planes is also accounted from the torsion angle data (Table 3, Fig. 3).

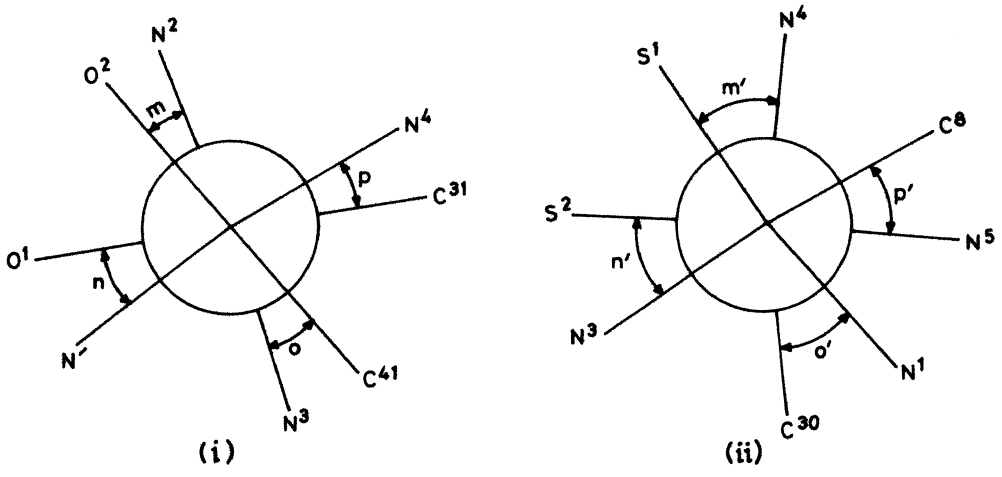

Fig. 3. Comparison of conformation angles for (i) **2a** and (ii) **3a**. For (i): (**2a**) m, −18.90; n, −17.45; o, −23.16; p, 23.17°. For (ii): (**3a**) m', −38.84; n', −38.44; o', −35.14; p', −34.27°.

Table 3
Some selective conformational and torsion angles

$[Pd(A_1)(\mu\text{-}N,O)]_2$ (**2a**)		$[Pd(A_1)(\mu\text{-}N,S)]_2$ (**3a**)	
N(1)–Pd(1)···Pd(2)	87.07(5)	N(3)–Pd(1)···Pd(2)	83.6(1)
O(2)–Pd(1)···Pd(2)	78.92(4)	S(1)–Pd(1)···Pd(2)	79.9(1)
C(41)–Pd(1)···Pd(2)	100.73(6)	C(8)–Pd(1)···Pd(2)	96.7(1)
N(4)–Pd(1)···Pd(2)	101.06(5)	N(1)–Pd(1)···Pd(2)	105.6(1)
Torsion angles			
Pd(1)–O(2)–C(21)–N(2)	−29.8(3)	Pd(1)–S(1)–C(13)–N(4)	−40.42
Pd(1)–N(1)–C(11)–O(1)	−6.9(3)	Pd(1)–N(3)–C(18)–S(2)	−15.94
Pd(2)–O(1)–C(11)–N(1)	−19.3(3)	Pd(2)–N(4)–C(13)–S(1)	−2.90
Pd(2)–N(2)–C(21)–O(2)	1.6(3)	Pd(2)–S(2)–C(18)–N(3)	−28.56
N(2)–Pd(2)–Pd(1)–O(2)	−18.90(7)	N(3)–Pd(1)–Pd(2)–S(2)	−38.44
N(3)–Pd(2)–Pd(1)–C(41)	−23.16(9)	N(5)–Pd(2)–Pd(1)–C(8)	−34.27
N(1)–Pd(1)–Pd(2)–O(1)	−17.45(7)	N(4)–Pd(2)–Pd(1)–S(1)	−38.84
N(4)–Pd(1)–Pd(2)–C(31)	−23.17(9)	N(1)–Pd(1)–Pd(2)–C(30)	−35.14

3.3. Spectral studies

The complexes display IR spectra characteristic to ν(N=N) at 1380–1385 cm^{-1} [7]. The assignment of all bands has not been attempted. However, a comparison of the spectra with those of the respective chloro-bridged dimers and of free 2-hydroxypyridine–2-mercaptopyridine affords useful information. Heterocyclic ring stretching in free ligand at 1608, 1420, 1240, 1155 cm^{-1} are shifted to higher energy region by 5−15 cm^{-1}. $[Pd(A)(\mu\text{-}N,O)]_2$ (**2**) exhibit stretching at 440−470 and 330−360 cm^{-1} corresponding to ν(Pd–O) and ν(Pd–N), respectively $[Pd(A)(\mu\text{-}N,S)]_2$ (**3**) exhibit ν(Pd–S) and ν(Pd–N) at 300–330 and 360–380 cm^{-1}, respectively. The solution spectra were recorded in 900−200 nm in chloroform and assigned on the basis of literature data [7]. Absorptions below 400 nm are due to intramolecular charge transfer transition and are not considered further. Out of two transitions in the visible region in 450−480 and 540−580 nm the first transition may be assigned to charge transfer in the metallated azo fragment, dπ(Pd) → azo(A) [9]. The second transition (longer wave length) is new and may be associated with charge transition in the bridged palladium(II)-heterocyclic unit.

The complexes display well resolved ^{1}H-NMR spectra in $CDCl_3$ which have been assigned on the basis of chemical shifts, spin–spin structure and the effect of substituents. The ^{1}H-NMR spectra of cyclopalladated complexes [7], serve as guide to the assignment of azobenzene protons in the present series of complexes. The atom numbering pattern is shown in Scheme 1. In case of unsymmetrical azobenzene (A_2/A_3), where the metallation of both substituted and unsubstituted rings occurs, the population of isomer having metallation in the substituted ring is higher in line with the electrophilic nature of the palladation reaction [29]. The intensity ratio of two -Me signals of $[Pd(A_2)(\mu\text{-}N,X)]_2$ (**2b/3b**): $[Pd(A_3)(\mu\text{-}N,X)]_2$ (**2b′/3b′**) is 2:1 and is in agreement with the reported results [7]. Symmetric azobenzenes (A_1, A_4, A_5) yield single mixed dimer and is supported by two -Me signals of equal intensity in $[Pd(A_4)(\mu\text{-}N,X)]_2$. Azobenzene protons perturb significantly by the substituents in the usual manner [27] and heterocyclic protons (13-H−16-H) are distinctly different and hardly affected by the substituents in the azobenzene ring. The ^{13}C-NMR spectra of the complexes are in agreement with the proposed structure.

3.4. Electrochemistry

The electrochemical studies of the complexes were carried out by cyclic voltammetry under N_2 environment using glassy carbon working electrode in acetonitrile solution. The redox potentials are expressed with reference to saturated calomel electrode (SCE) in presence of *n*-tetrabutylammoniumperchlorate [*n*-Bu_4N][ClO_4]. The IR compensation was applied internally in the instrument. All the complexes display two redox responses (Fig. 4). The peak potentials are nearly invariant with scan rate (50−500 mV s^{-1}). First couple appears at −0.6 to −0.8 V for $[Pd(A)(\mu\text{-}N,O)]_2$ (**2**) and −0.7 to −0.9 V for $[Pd(A)(\mu\text{-}N,S)]_2$ (**3**) and is quasi-reversible as it evident from peak-to-peak separation (ΔE_p = 70–90 mV). The second redox response is irreversible in nature (ΔE_p = 120 mV) and appears at more negative value (> −1.1 V). The cathodic peak current (i_{pc}) is proportional to $v^{1/2}$ and i_{pa}/i_{pc} lies at 0.93−1.04 suggesting reversibility of the redox process. The current height measurement exhibits one-electron redox process. The reduction is believed to be the accommodation of electron at LUMO characterised by azo group [7]. The half wave potential ($E_{1/2}$) moves to negative value with electron donating substituent(s) in the aryl ring and reverse movement is observed for electron withdrawing group. The second response is irreversible and does not conform to the second step reduction of azo function [17]. The reduction of hetero-

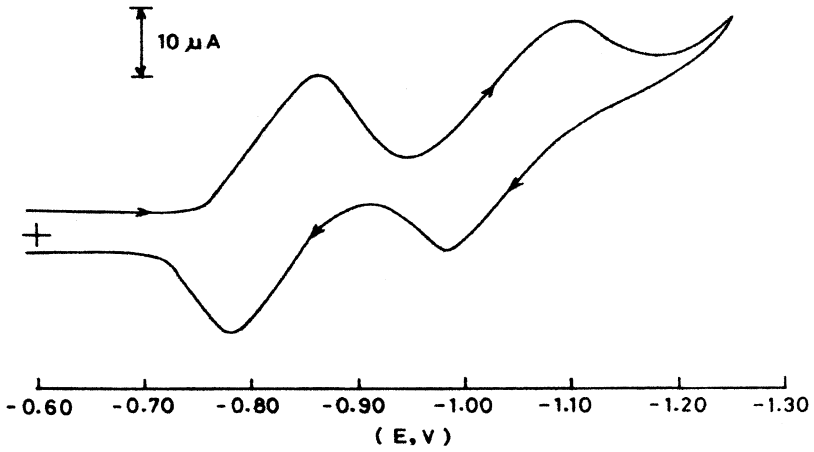

Fig. 4. Cyclic voltammogram of $Pd(A_2)(\mu\text{-}N,O)]_2$ in MeCN using Pt-millielectrode and $[n\text{-}Bu_4N][ClO_4]$ as supporting electrolyte at 298 K.

cyclic coligand is not ruled out which may need comparatively higher energy to accommodate electrons at the antibonding orbital. There may be a certain degree of involvement of coligand π-orbital in conjunction with azo-anti bonding orbital.

4. Supplementary materials

Atomic coordinates H-atom coordinates, thermal parameters, a complete list of bond distances and angles, and lists of structure factors are available from the CCDC, 12, Union Road, Cambridge CB 2 1EZ, UK on request and the deposition numbers are 147256 for **2a** and 156639 for **3a**.

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