

# Synthesis and Characterization of Some Dimeric Platinum Metal Complexes with N,N,N',N'-*Tetrakis*(2-pyridylmethyl)benzene-1,4-diamine

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Dinuclear platinum metal complexes  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where, M = Pd or Pt and 1,4-tpbd = N,N,N',N'-*tetrakis*(2-pyridylmethyl)benzene-1,4-diamine),  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$  and  $[Rh_2(1,4-tpbd)(PPh_3)_2Cl_2]$  were synthesized from their precursors PdCl\_2, K\_2PtCl\_4,  $[Ru(DMSO)_4Cl_2]$  and  $[Rh(PPh_3)_3Cl_2]$  respectively. The composition and the expected structures of the complexes have been discussed in view of their data obtained from various analytical, magnetic moment, molar conductance, UV-visible, FT-IR and <sup>1</sup>H NMR spectroscopic studies.  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where, M = Pd or Pt) complexes were expected to have distorted square-planar geometries, in which the coordination of the ligand 1,4-tpbd to the metal ions occurs through all the N atoms in a *bis*-tridentate bridging fashion. The complex  $[Rh_2(1,4-tpbd)(PPh_3)_2Cl_2]$ , a square-planar geometry was proposed, in which the ligand 1,4-tpbd bonded through two N-atoms of the picolyl group, one chlorine atom and one triphenylphosphine group per rhodium atom. An octahedral structure was proposed to the complex  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$ . The electronic spectra of all the complexes were dominated by strong charge transfer bands indicative of binding of 1,4-tpbd ligand in a bridging manner to the metal centers. For the  $[Rh_2(1,4-tpbd)(PPh_3)_2Cl_2$  complex in dichloromethane, a reversible peak at  $E_{v_2} = 0.39$  V and  $\Delta E_p = 80$  mV was observed, which may be assigned to two electrons Rh<sup>1</sup>/Rh<sup>III</sup> oxidation couple.

Keywords: Dimeric, N,N,N',N'-Tetrakis(2-pyridylmethyl)benzene-1,4-diamine), UV-visible, <sup>1</sup>H NMR, Cyclic voltammetry.

## **INTRODUCTION**

Complexes containing polypyridyl chelating ligands have been extensively studied in the recent past [1-5]. The rich photo-physical and redox properties make them potentially useful in areas as diverse as light harvesting, electron transfer, non-linear optics, photo-voltaics, self-assembly and probes for biologically relevant molecules such as DNA [6-10]. The chemistry of metal complexes with *bis*-tridentate ligand *e.g.* N,N,N',N'-tetrakis(2-pyridylmethyl)benzene-1,4-diamine (1,4-tpbd) (Fig. 1) has received attention after it's discovery by Buchen et.al. [11] and introduced it to build up defined polynuclear coordination systems [10]. Beside some mononuclear complexes of 3d transition metals and one polynuclear Pd-containing complex [11-14] only four multinuclear complexes have been reported by McKenzie et al. [14(a)-(d)]. In all these complexes 1,4-tpbd acts either as a tridentate ligand or a bridging bis-tridentate ligand between two metal centres.



Fig. 1. Structure of N,N,N',N'-*tetrakis*(2-pyridylmethyl)benzene-1,4diamine (1,4-tpbd)

In view of the above importance of the platinum metal complexes with 1,4-tpbd ligand, the present work describes the synthesis, characterization and structural elucidation of some dinuclear platinum metal complexes with the 1,4-tpbd ligand which is bonded either in a bridged *bis*-tridentate or *bis*-bidentate fashion to the metal centers. Here in, we report

the synthesis and characterization of Pd(II) and Pt(II) complexes with the ligand 1,4-tpbd and Ru(II) and Rh(I) complexes with 1,4-tpbd containing either dimethyl sulphoxide or triphenylphoshine as co-ligand, respectively.

## **EXPERIMENTAL**

All the chemicals used are of AR or chemically pure grade. Solvents were purified prior to use by standard methods. K<sub>2</sub>[PtCl<sub>4</sub>] and PdCl<sub>2</sub> were purchased from Merck. cis-[Ru(DMSO)<sub>4</sub>Cl<sub>2</sub>] and [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] were prepared according to reported procedure [14(e),(d)]. 2-Picolylchloride hydrochloride was purchased from Sigma Aldrich. The ligand 1,4tpbd was prepared as per reported method [11]. CHN analyses were carried out at SAIF, NEHU, Shillong. The analytical data were presented in Table-1. Infrared spectra were recorded using KBr pellets on a Perkin-Elmer 983 spectrophotometer in the region 4000-300 cm<sup>-1</sup>. <sup>I</sup>H NMR, spectra were recorded on a Brucker ACF 300 spectrometer from SAIF, NEHU, Shillong. The electronic spectra were recorded in dimethyl sulphoxide on a Perkin Elmer Lamda 25 spectrophotometer in the region 800-300 nm. The <sup>1</sup>H NMR spectral data and electronic absorption maximum bands of the complexes were presented in Table-2. The cyclic voltammetric studies were carried out using CH instruments electrochemical analyzer CHI 620B under nitrogen atmosphere. The measurments of the complexes were performed in dimethyl sulphoxide  $(10^{-3} \text{ M})$  employing tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte in a three electrode configured electrolytic cell. The working electrode was a glassy carbon disk from BAS and the reference electrode was a aqueous SCE or Ag/AgCl separated from the sample solution by a salt bridge. All potential were determined vs. SCE at  $25 \pm 2$  °C and are uncorrected for junction potential. Spectroscopic grade solvents were used for cyclic voltammetry and UV-visible measurements. Magnetic susceptibilities of the complexes were measured on an EG & G PARC vibrating sample magnetometer model 155 at room temperature in powder form. Molar conductivity measurements were made on a Wayne-Kerr Automatic Precision B905 conductivity meter with millimolar solution in acetonitrile or dimethyl sulphoxide (NEHU, Shillong).

Synthesis of  $[Pd_2(1,4-tpbd)Cl_2]Cl_2$ : To a clear solution of PdCl<sub>2</sub> (0.180 g; 1.01 mmol) in acetonitrile (25 cm<sup>3</sup>) obtained after refluxing for 15 min on a water bath, the ligand (L) 1,4tpbd (0.475 g; 1.01 mmol) was added to the solution in a molar ratio (Pd:L) 1:1. The mixture was refluxed for another 4 h. On cooling the solution at room temperature, a yellow coloured compound separated out which was isolated by centrifugation and washed with diethyl ether several times and dried *in vacuo*. Yield: (0.245 g) 58 %;  $\Lambda_M = 45 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ; IR (KBr,  $\nu_{max}$ , cm<sup>-1</sup>): 3462 (br), 3065 (m), 2945 (m), 1606 (s), 1507 (m), 1493 (s), 1447 (m), 1288 (w), 1169 (w), 1062 (w), 771 (s).

Synthesis of  $[Pt_2(1,4-tpbd)Cl_2]Cl_2$ : An aqueous solution (5 cm<sup>3</sup>) of K<sub>2</sub>[PtCl<sub>4</sub>] (0.207g; 0.55 mmol) was treated with a methanolic solution (20 cm<sup>3</sup>) of 1,4-tpbd (L) (0.260 g; 0.55 mmol) in a molar ratio (Pt:L) 1:1 and the mixture was magnetically stirred at room temperature for 2 h. When the colour of the solution changed from red to yellow, a yellow colour precipitate obtained which was separated out by

centrifugation and washed with diethyl ether several times and dried *in vacuo*. Yield: (0.186 g) 67 %;  $\Lambda_M$ : 45.82  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; IR (KBr,  $\nu_{max}$ , cm<sup>-1</sup>): 3456 (br), 3058 (m), 2925 (m), 1613 (s), 1520 (s), 1427 (m), 1361 (m), 1295 (w), 1248 (m), 1202 (w), 1029 (w), 767 (s).

Synthesis of  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$ : *cis*-[Ru(DMSO)<sub>4</sub>Cl<sub>2</sub>] (0.490 g; 1.01 mmol) dissolved in methanol (20 cm<sup>3</sup>) by stirring the solution at room temperature for 10 min. To that solution solid 1,4-tpbd (L) (0.475 g; 1.01 mmol) was added and the mixture was further stirred at room temperature for another 2 h. A yellow colour precipitate was obtained, which was isolated by centrifugation, washed several times with diethyl ether and dried *in vacuo*. Yield: (0.252 g) 51 %;  $\Lambda_{M}$ : 11.10  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; IR (KBr,  $\nu_{max}$ , cm<sup>-1</sup>): 3420 (br), 3053 (m), 2922 (m), 1615 (s), 1517 (s), 1481 (m), 1435 (s), 1352 (m), 1286 (w), 1189 (m), 1118 (s), 1091 (m), 766 (s), 696 (s), 541 (m), 519 (s), 435 (m).

Synthesis of [Rh<sub>2</sub>(1,4-tpbd)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]: [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] (0.235 g; 0.25 mmol) was dissolved in benzene (25 cm<sup>3</sup>) by heating on a water-bath for 0.5 h. To a clear solution, solid 1,4-tpbd (L) (0.120 g; 0.25 mmol) was added and the mixture was stirred at room temperature for 18 h. A red colour compound separated out, which was isolated by centrifugation and washed several times with diethyl ether and dried *in vacuo*. Yield: (0.102 g) 63 %;  $\Lambda_{\rm M}$ : 12.71  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; IR (KBr,  $\nu_{\rm max}$ , cm<sup>-1</sup>): 3423 (br), 3237 (m), 2925 (s), 1600 (s), 1520 (s), 1474 (m), 1434 (s), 1354 (m), 1261 (w), 1116 (m), 1029 (w), 760 (s), 698 (m), 545 (w).

### **RESULTS AND DISCUSSION**

The compounds  $PdCl_2$  and  $K_2[PtCl_4]$  were used as precursor for the synthesis of Pd(II) and Pt(II) complexes of the type  $[M_2(1,4-tpbd)Cl_2]Cl_2$  [where M = Pd or Pt:1,4-tpbd = N,N,N',N'-*tetrakis*-(2-pyridylmethyl)-benzene-1,4-diamine)] in acetonitrile and methanolic medium respectively either under refluxing condition or at room temperature. Complexes of the type  $[M_2(1,4-tpbd)(L)_2Cl_n]$  (when M = Ru; L = DMSO; n = 4 or M = Rh; L = PPh\_3; n = 2) were prepared by a reaction of  $[Ru(DMSO)_4Cl_2]$  or  $[Rh(PPh_3)_3Cl]$  with 1,4-tpbd in methanol or benzene respectively by stirring at room temperature.

All the complexes obtained were yellow in colour except  $[Rh_2(1,4-tpbd)(PPh_3)_3Cl_2]$ , which was red in colour. The complexes synthesized were air-stable but decomposes or melt in the temperature range of 220-270 °C. Micro-analytical data (Table-1) obtained were in conformity with the composition  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where M = Pd or Pt) and  $[M_2(1,4-tpbd)(L)_2Cl_n]$  (when M = Ru; L = DMSO; n = 4 or M = Rh; L = PPh\_3; n = 2). The solubility of Pd(II) and Pt(II) complexes were found very low in common organic solvents such as methanol, ether, chloroform, dichloromethane, *etc.* but they were soluble in high boiling solvents *viz.* dimethyl sulphoxide or N,N'-dimethyl formamide. The Ru(II) and Rh(I) analogues were soluble in common organic solvents.

**Molecular weight:** The molecular weight of the complexes (Table-1) have been determined in spectral grade DMSO by the freezing point depression method. The experimental values of molecular weight for the complexes were found close to the calculated values based on their dimeric formulae thereby

| TABLE-1<br>ANALYTICAL RESULTS OF SOME PLATINUM METAL COMPLEXES CONTAINING 1,4-tpbd |        |           |                  |  |             |             |               |  |
|--|--------|-----------|------------------|--|-------------|-------------|---------------|--|
| Complex  | Colour | m.p. (°C) | m.w. (calcd.)    | Elemental analysis (%): Found (calcd.) |             |             |               |  |
|  |        |           |                  | С                                      | Н           | Ν           | Cl            |  |
| [Pd <sub>2</sub> (1,4-tpbd)Cl <sub>2</sub> ]Cl <sub>2</sub>                        | Yellow | 264       | 965 ± 80 (827)   | 43.25 (43.54)                          | 3.08 (3.39) | 10 (10.16)  | 16.77 (17.17) |  |
| [Pt <sub>2</sub> (1,4-tpbd)Cl <sub>2</sub> ]Cl <sub>2</sub>                        | Yellow | 270       | 1184 ± 90 (1004) | 35.45 (35.85)                          | 2.55 (2.79) | 8.20 (8.37) | 13.77 (14.14) |  |
| [Ru <sub>2</sub> (1,4-tpbd)(DMSO) <sub>2</sub> Cl <sub>4</sub> ]                   | Yellow | 220       | 1050 ± 75 (927)  | 41.45 (41.97)                          | 3.95 (4.12) | 8.42 (8.64) | 14.27 (14.61) |  |
| $[Rh_2(1,4-tpbd)(PPh_3)_2Cl_2]$  | Red    | 232       | 1315 ± 35 (1273) | 62.05 (62.23)                          | 4.21 (4.56) | 6.42 (6.60) | 5.17 (5.58)   |  |

confirming that they are dimeric in nature. However, the experimental values of molecular weight for the complexes  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where M = Pd or Pt) obtained were slightly higher than those calculated values which strongly suggest that structure of these dimeric complexes were altered in the coordinating solvent as compared to that in the solid state. Most probably, the coordinated chlorine are substituted by the DMSO molecules, which may accounts for their higher molecular weights of the complexes [15].

Molar conductance: In view of the above observation, conductivity measurement of complexes [M2(1,4-tpbd)Cl2]Cl2 (where M = Pd or Pt) were carried out in a milimolar concentration using DMSO as solvent. The molar conductance values for the complexes  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where M = Pd or Pt) obtained were in the range of 45-48  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> which is somewhat less than that for 1:2 electrolytes but more than 1:1 electrolyte in DMSO [15]. The lower values suggests that it may be due to either solvent interactions or low ionic mobility of the chloride ion in the solvent [16]. Thus a coordination structure of the type  $[M_2(1,4-tpbd)Cl_2]Cl_2$  is proposed. The molar conductance values for the  $[M_2(1,4-tpbd)(L)_2Cl_n]$  (when  $M = Ru; L = DMSO; n = 4 \text{ or } M = Rh; L = PPh_3; n = 2)$  complexes in acetonitrile are 11  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> and 12.7  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> for Ru(II) and Rh(I) complexes respectively, thereby confirming the covalent nature of the chlorido groups in the complexes [16].

**Magnetic moment:** The magnetic susceptibility values obtained for all the complexes at 25 °C showed diamagnetic behaviour thereby confirming low spin  $d^8$  configuration for Pd(II), Pt(II) and Rh(I) in [M<sub>2</sub>(1,4-tpbd)Cl<sub>2</sub>]Cl<sub>2</sub>] (where M = Pd or Pt) and [Rh<sub>2</sub>(1,4-tpbd)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complexes respectively and a low spin  $d^6$  configuration for Ru(II) in [Ru<sub>2</sub>(1,4-tpbd) (DMSO)<sub>2</sub>Cl<sub>4</sub>] complex.

Infrared spectra: Infrared spectral data of the complexes  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where M = Pd or Pt; 1,4-tpbd = N,N,N',N'-*tetrakis*(2-pyridylmethyl)benzene-1,4-diamine),  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$  and  $[Rh_2(1,4tpbd(PPh_3)_2Cl_2]$  were in conformity with their composition and also confirms the binding mode of the N-donor bridging 1,4-tpbd ligand. Significant infrared spectral bands of DMSO and PPh3 as co-ligands in the Ru(II) and Rh(I) complexes respectively were also present thereby confirming their presence in the complexes. All the complexes showed in common one strong absorption band each in the region 1620-1600, 1520-1500 and 780-760 cm<sup>-1</sup> which may be due to the presence of coordinated N-donor 1,4-tpbd ligand [11]. In the Ru(II) analogue, one strong and one medium absorption band at 1118 and 435 cm<sup>-1</sup> were also observed which were attributable to v(S=O) of the S-bonded DMSO and v(Ru-S) respectively [17,18]. Since no strong band in the region 1000-900 cm<sup>-1</sup> were observed thereby confirming the presence of S-bonded DMSO group. The Rh(I) complex, in addition to absorption bands due to 1,4-tpbd ligand showed one strong absorption band at 1474 cm<sup>-1</sup> and one medium intensity band at 1434 cm<sup>-1</sup>, besides these absorption bands two more characteristic bands at 1116 and 1029 cm<sup>-1</sup> were also observed which confirms the presence of coordinated triphenylphosphine molecule to the central metal atom [19].

**Electronic spectra:** The electronic absorption spectra of the  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where M = Pd or Pt),  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$  and  $[Rh_2(1,4tpbd(PPh_3)_2Cl_2]$  complexes showed one strong absorption band between 437-416 nm with  $\bigcirc$  in the range  $6.32 \times 10^2$  to  $1.38 \times 10^3$ , which may be assigned to metal to ligand charge transfer type of transition (Table-1) [19,20]. Two more additional bands in the complexes  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$  and  $[Rh_2(1,4tpbd(PPh_3)_2Cl_2]$  were observed with  $\in$  of the order of 10<sup>3</sup> in the range 380-355 nm and 272-260 nm which may be assignable to  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  intra ligand charge transfer transition [11].

Cyclic voltammetry: The cyclic voltammetric behaviour of the dinuclear complex [Ru2(1,4-tpbd)(DMSO)2Cl4] in acetonitrile using tetrabutylammonium perchlorate as supporting electrolyte is characterized by a quasi-reversible peak at  $E_{\frac{1}{2}}$  =  $0.57 \text{ V} (\Delta E_p = 250 \text{ mV})$  which may be attributable to  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ oxidation couple [21]. On varying scan rate from 0.02 to 0.20 V s<sup>-1</sup>, a change of  $\Delta E_p$  from 160-250 mV were obtained, whereas  $E_{1/2}$  remains constant thereby confirming quasi-reversibility of the system. The cyclic voltammogram of [Rh<sub>2</sub>(1,4tpbd)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complex (Fig. 2) in dichloromethane show one reversible oxidation potential at  $E_{\frac{1}{2}} = 0.39$  V, which may be assigned to Rh<sup>III</sup>/Rh<sup>I</sup> oxidation couple [Fig. 2].  $\Delta E_p$  for the Rh(I) complex is observed at 80mV which does not change on varying scan rate 0.02 to 0.20 V s<sup>-1</sup> is indicative of two electron transfer system hence  $\Delta E_p$  for one electron transfer will be equal to 40 mV which is in conformity with the reversible nature of the redox couple [22].

The cyclic voltammetric studies of  $[M_2(1,4-tpbd)Cl_2]Cl_2$ (where M = Pd or Pt) in dimethyl sulphoxide showed one reduction wave at potential -1.2 and -1.0 V respectively which may be due to the reduction of the ligand (1,4-tpbd).

**NMR spectra:** The <sup>1</sup>H NMR spectra of the complexes  $[M_2(1,4-tpbd)Cl_2]Cl_2$  (where M = Pd or Pt) (Fig. 2) and  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$  in DMSO-*d*<sub>6</sub> showed one singlet in the region  $\delta$  5.07-4.88 which may be assigned to eight methylene protons of the 1,4-tpbd ligand. The presence of one singlet due to methylene protons in the complexes were shifted towards downfield by  $\delta$  0.18-0.37 in compare to the free ligand 1,4-tpbd, which suggest that the 1,4-tpbd ligand is coordinated to the metal center through all the N-atom present in it. Further the presence of singlet at  $\delta$  4.69 for the complex [Rh<sub>2</sub>(1,4-tpbd)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (Table-2), attributable to methylene protons



Fig. 2. Cyclic voltammetry of  $[Rh_2(1,4-tpbd)(PPh_3)_2Cl_2$  in dichloromethane at room temperature under N<sub>2</sub>-atomsphere using TBAP as supporting electrolyte at scan rate 0.1 V/s

observed at the same position as in the free 1,4-tpbd ligand. The unusual downward shift of methylene protons of the 1,4-tpbd ligand is indicative of the N-atom neighboring methylene groups may not be coordinated to the rhodium atom.

All the complexes showed two doublets in the region  $\delta$  8.48-8.88 and  $\delta$  7.28-7.75 and two triplets in the region  $\delta$  7.64-8.08 and  $\delta$  7.14-7.65, which may be attributable to the protons of the picolyl group. Protons signals due to picolyl groups in case of all the complexes, are shifted to downfield compared to the free ligand, thereby confirming the coordination of picolyl N-atoms in all the complexes to the metal ions. Also in the region  $\delta$  5.94-6.56, one double doublet is observed in all the complexes attributable to the aromatic protons of 1,4-tpbd. The ratio between aromatic protons and methylene protons observed is 1:2 which is indicative of the presence of four aromatic protons and eight methylene protons in the 1,4-tpbd ligand.

Furthermore, in the complex [Ru<sub>2</sub>(1,4-tpbd)(DMSO)<sub>2</sub>Cl<sub>4</sub>], one singlet at  $\delta$  3.53, assignable to the methyl protons of dimethyl sulphoxide is also observed. The shift for the singlet signal from lower  $\delta$  2.30 value for free dimethyl sulphoxide group to higher suggests that the dimethyl sulphoxide coordinated to the metal center through the sulphur atom [17,23]. In the region  $\delta$  7.45-7.66 multiplets observed are attributable to triphenylphosphine in [Rh<sub>2</sub>(1,4-tpbd)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] complex, which is assigned to triphenylphosphine ligands. The proton signal ratio between 1,4-tpbd and triphenylphosphine observed are almost same which confirms the presence of two triphenylphosphine molecules with respect to one bridging 1,4-tpbd ligand. The <sup>1</sup>H NMR data of all the complexes were presented in Table-2. **Structural elucidation:** On the basis of the observations in physical and analytical study of the complexes of Pd(II) and Pt(I) with 1,4-tpbd, the following structure may be proposed, where overall geometry around the central metal atom is distorted square planar (Fig. 3).



Fig. 3. Proposed structure of Pd(II) and Pt(II) complex with 1,4-tpbd, Where M = Pd(II) or Pt(II)

In  $[Ru_2(1,4-tpbd)(DMSO)_2Cl_4]$  complex the chloride group may be bonded to the Ru atom either in a *cis* or *trans* fashion, therefore the structure of the complex may be proposed as distorted octahedral as shown below (Fig. 4).



Fig. 4. Structure of cis-[Ru<sub>2</sub>(1,4-tpbd)(DMSO)<sub>2</sub>Cl<sub>4</sub>] complex with 1,4-tpbd

The  $[Rh_2(1,4-tpbd)(PPh_3)_2Cl_2]$  complex, where the ligand 1,4-tpbd is bonded to rhodium atom through two N-atoms of the picolyl group hence a square planar geometry may be assigned to the complex as shown in Fig. 5.



Fig. 5. Structure of [Rh2(1,4-tpbd)(PPh3)2Cl2] complex with 1,4-tpbd

| TABLE-2   |   |  |  |  |  |  |
|---|---|--|--|--|--|--|
| <sup>1</sup> H NMR AND UV-VISIBLE SPECTRAL DATA OF COMPLEXES  |   |  |  |  |  |  |
| Complex   | <sup>1</sup> H NMR (ppm)  | UV-visible $(\lambda_{max} nm, \in)$   |  |  |  |  |
| [Pd <sub>2</sub> (1,4-tpbd)Cl <sub>2</sub> ]Cl <sub>2</sub> <sup>a</sup>  | 5.07(s), 5.94(dd), 7.59(t), 7.69(d), 8.17(t), 8.48(d)               | 416(1.385×10 <sup>3</sup> )  |  |  |  |  |
| [Pt <sub>2</sub> (1,4-tpbd)Cl <sub>2</sub> ]Cl <sub>2</sub> <sup>a</sup>  | 4.88(s), 6.37(dd), 7.57(t), 7.66(d), 8.09(t), 8.83(d)               | 432(1.507×10 <sup>3</sup> )  |  |  |  |  |
| [Ru <sub>2</sub> (1,4-tpbd)(DMSO) <sub>2</sub> Cl <sub>4</sub> ] <sup>a</sup>   | 3.53(s), 4.91(s), 6.29(dd), 7.65(t), 7.75(d), 8.19(t), 8.88(d)      | 437sh, (6.84×10 <sup>2</sup> ), 380(1.66×10 <sup>3</sup> ), 260(1.73×10 <sup>3</sup> ) |  |  |  |  |
| $[Rh_2(1,4\text{-tpbd})(PPh_3)_2Cl_2]^b$  | 4.69(s), 6.56(dd), 7.14(t), 7.28(d), 7.64(t), 7.66-7.45(m), 8.55(d) | 436sh, (6.32×10 <sup>2</sup> ), 355(8.90×10 <sup>3</sup> ), 272(1.60×10 <sup>3</sup> ) |  |  |  |  |
| where <sup>a</sup> In DMSO- $d_{6s}$ <sup>b</sup> In CDCl <sub>3</sub> s = Singlet, d = Doublet, t = Triplet, sh = Shoulder |   |  |  |  |  |  |

#### Conclusion

The dinuclear bridging complexes of Pd(II), Rh(I), Pt(II) and Ru(II) were synthesized from 1,4-tpbd. Rh(I) complex show reversible one electron redox couple which may be assigned to Rh<sup>I</sup>/Rh<sup>III</sup> oxidation couple. The tentative geometry around the Pd(II), Rh(I) or Pt(II) proposed to have distorted square-planar geometry. In Rh(I) complex methylene N-atom is not co-ordinated to metal centre. For complex [Ru<sub>2</sub>(1,4tpbd)(DMSO)<sub>2</sub>Cl<sub>4</sub>] the structure is proposed octahedral with three N-atoms, one S-bonded dimethyl sulphoxide and two chloro group as two chloro group may be *cis* or *trans* position.

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