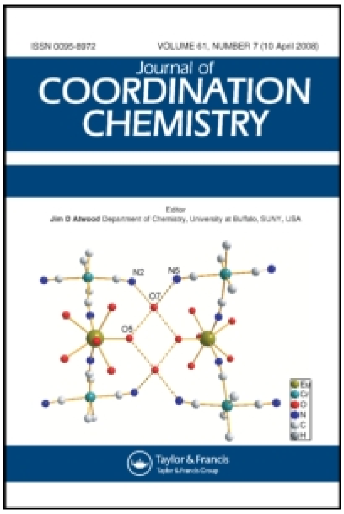

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Ruthenium(II) and palladium(II) complexes with 2,6-(bispyrazol-1-yl)pyridines

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To cite this Article Chakrabarty, Surajit , Sarkhel, Prashanta and Poddar, Raj K.(2010) 'Ruthenium(II) and palladium(II) complexes with 2,6-(bispyrazol-1-yl)pyridines', Journal of Coordination Chemistry, 63: 9, 1563 — 1569, First published on: 29 April 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.482153

URL: http://dx.doi.org/10.1080/00958972.2010.482153

Journal of Coordination Chemistry
Vol. 63, No. 9, 10 May 2010, 1563–1569

Ruthenium(II) and palladium(II) complexes with 2,6-(bispyrazol-1-yl)pyridines

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(*Received 25 May 2009; in final form 20 January 2010*)

Ruthenium(II) and palladium(II) complexes [Ru(DMSO)(L)Cl_2] and [Pd(L)Cl]Cl, where L = 2,6-bis(pyrazol-1-yl)pyridine (bpp) or 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (bdmpp) have been synthesized. All complexes were characterized by elemental analysis, IR, ^{1}H NMR, UV-Vis, and cyclic voltammetry measurements.

Keywords: Ruthenium(II); Palladium(II); Tripodal; ^{1}H NMR; UV-Vis; Cyclic voltammetry

1. Introduction

Tripodal ligands are of interest due to the coordinating ability toward metal ions [1–11]. Transition metal complexes with the tripodal ligands, namely, 2,6-bis(pyrazol-1-yl) pyridine (bpp) and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (bdmpp) (figure 1) display interesting physical, chemical, magnetic, structural, and catalytic properties. They also form various supramolecular complexes and generally show high thermodynamic stability and kinetic inertness [12–23]. There is considerable interest in the photophysical, photochemical, and redox properties of these complexes [12, 14, 15, 17].

Complexes of ruthenium(II) with bpp and bdmpp are of the type $[RuL_2]^{2+}$, [RuLCl_3], [RuL(PMe_3)Cl_2], [RuL$(PMe_3)_2$Cl](ClO_4), *trans*-[Ru(L)(NO_2)$(PMe_3)_2$]ClO_4, [RuL(β-diketonate)]Cl (where L = bpp or bdmpp; β-diketonate = 1,3-substituted β-diketonate), *cis*- and *trans*-[RuCl$(PPh_3)_2$(bpp)]Cl, *trans*-[RuCl_2(bdmpp)(E)] (where E = PPh_3, C_2H_4, CO, CH_3CN, or =C=CPh_2) and [RuCl(PPh_3)(=C=C=CPh_2)(bdmpp)]BF_4. In all these complexes bpp and dmbpp are tridentate [12, 13, 18, 24].

The only palladium complex reported with bpp or bdmpp is [Pd(Me)(bpp)]OTos (OTos = tosylate). From ^{1}H NMR spectra bpp is reported as bidentate with the fourth coordination site occupied by tosylate or solvent [25]. Complexes of bpp and dmbpp with Pt(II) are [Pt(L)Cl]Cl $\cdot$ H_2O and [Pt(L)(Ph)]PF_6 (where L = bpp or bdmpp).

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.482153

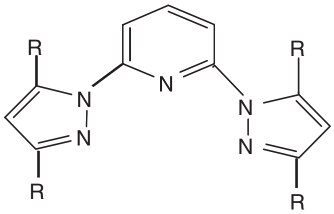

Figure 1. Structure of bpp and bdmpp, R = H, bpp; R = CH_3, bdmpp.

Structures of the bpp analogue of the two types of complexes have been determined by X-ray crystallography, wherein bpp is tridentate to Pt through two pyrazolyl nitrogens and the pyridine nitrogen to give nearly a planar Pt(bpp). The fourth coordination site was occupied by Cl^- or Ph [19].

In our previous work synthesis, the characterization and single crystal X-ray structures of Cu(II) complexes $[CuBr_2(bpp)]$ and $[Cu_2Br_2(bpp)_2](ClO_4)_2$ have been reported [26]. This work describes the synthesis, characterization, and structural assessments of Ru(II) and Pd(II) complexes with bpp or bdmpp.

2. Experimental

All chemicals used are of AR or chemically pure grade. Solvents were purified prior to use by standard methods. 2,6-Dibromopyridine, pyrazole, and $PdCl_2$ were purchased from Merck. 3,5-Dimethylpyrazole was prepared by the condensation of acetylacetone and hydrazine hydrate. The ligands bpp and bdmpp were prepared according to published procedure [27]. *Cis*-$[Ru(DMSO)_4Cl_2]$ was prepared as reported [28]. Molar conductivity measurements of millimolar solutions were made on a Wayne–Kerr Automatic precision B905 conductometer. IR spectra were recorded as KBr pellets using a Perkin-Elmer spectrum BX series spectrophotometer. C, H, and N analyses were carried out at SAIF, NEHU, Shillong. Spectroscopic grade solvents were used for cyclic voltammetry and UV-Vis measurements. UV-Vis spectra were recorded on a Perkin-Elmer Lamda 25 spectrophotometer. Cyclic voltammetry measurements were carried out on a CH instruments electrochemical analyzer CHI 620B. ^1H NMR spectra were obtained from NMR Instrumental Facility, IISc, Bangalore, India. Room temperature magnetic measurement of the complexes was carried out on a Sherwood Scientific magnetic susceptibility balance.

2.1. *Preparation of [Ru(DMSO)(bpp)Cl₂]*

A solution of *cis*-$[Ru(DMSO)_4Cl_2]$ (0.48 g, 1.00 mmol) and bpp (0.21 g, 1.00 mmol) in ethanol (25 cm^3) was refluxed for 2 h. A reddish solution was obtained and an oily mass was separated after removing the solvent under reduced pressure. The crude product was dissolved in dichloromethane. After addition of hexane, a red crystalline compound was obtained which was separated by centrifugation, washed several times with diethyl ether, and dried *in vacuo*. Yield = 0.30 g (65%). Anal. Calcd for $C_{13}H_{15}N_5SORuCl_2$ (%):

C, 33.84; H, 3.25; N, 15.18. Found (%): C, 34.07; H, 3.43; N, 15.44. IR (cm^{-1}, KBr pellets): 3098(m), 2919(m), 1487(s), 1089(s), 1016(m). Λ_M (DMSO): 14 Ω^{-1} cm^2 mol^{-1}.

2.2. *Preparation of [Ru(DMSO)(bdmpp)Cl$_2$]*

A mixture of *cis*-[Ru(DMSO)$_4$Cl$_2$] (0.48 g, 1.00 mmol) and bdmpp (0.27 g, 1.00 mmol) in ethanol (25 cm^3) was refluxed for 3 h. The solution changed from yellow to orange, the solvent was removed under reduced pressure producing an orange compound which then was washed several times with diethyl ether and dried *in vacuo*. Yield = 0.31 g (60%). Anal. Calcd for $C_{17}H_{23}N_5SORuCl_2$ (%): C, 39.46; H, 4.45; N, 13.54. Found (%): C, 39.73; H, 4.77; N, 13.76. IR (cm^{-1}, KBr pellets): 3098(m), 2925(m), 1474(s), 1102(s), 1029(s), 875(m). Λ_M (DMSO): 12 Ω^{-1} cm^2 mol^{-1}.

2.3. *Preparation of [Pd(bpp)Cl]Cl*

$PdCl_2$ (0.18 g, 1.00 mmol) was dissolved in acetonitrile (20 cm^3) by refluxing for about 15 min. A solution of bpp (0.21 g, 1.00 mmol) in acetonitrile (10 cm^3) was added to the refluxing solution and refluxed for 2 h when a pink compound separated out. It was centrifuged, washed with diethyl ether and dried *in vacuo*. Yield = 0.18 g (46%). Anal. Calcd for $C_{11}H_9N_5PdCl_2$ (%): C, 34.02; H, 2.31; N, 18.04. Found (%): C, 34.05; H, 2.07; N, 17.75. IR (cm^{-1}, KBr pellets): 3085(m), 3045(m), 1487(s), 1102(s), 1062(m). Λ_M (DMSO): 20 Ω^{-1} cm^2 mol^{-1}.

2.4. *Preparation of [Pd(bdmpp)Cl]Cl*

$PdCl_2$ (0.18 g, 1.00 mmol) was dissolved in acetonitrile (20 cm^3) by refluxing for about 15 min. A solution of bdmpp (0.27 g, 1.00 mmol) in acetonitrile (10 cm^3) was added to the refluxing solution and refluxed for 2 h when the color of the solution changed from red to pink. A pink compound separated and was isolated by centrifugation, washed with diethyl ether and dried *in vacuo*. Yield = 0.21 g (47%). Anal. Calcd for $C_{15}H_{17}N_5PdCl_2$ (%): C, 40.54; H, 3.82; N, 15.76. Found (%): C, 40.45; H, 3.65; N, 15.80. IR (cm^{-1}, KBr pellets): 3091(m), 1487(s), 1062(m), 850(w). Λ_M (DMSO): 23 Ω^{-1}cm^{2}mol^{-1}.

3. Results and discussion

3.1. *Ruthenium(II) complexes with 2,6-bis(pyrazol-1-yl)pyridine (bpp) or 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (bdmpp) and dimethyl sulfoxide*

A reaction of *cis*-[Ru(DMSO)$_4$Cl$_2$] with tridentate ligand L (L = bpp or bdmpp) in ethanol yielded [Ru(DMSO)LCl$_2$] (where L = bpp or bdmpp). Microanalytical data are in conformity with the composition [Ru(DMSO)LCl$_2$]. Conductivity measurements in millimolar solution of these complexes in acetonitrile showed molar conductance of 12–15 Ω^{-1} cm^2 mol^{-1}, which are very low compared with 120 Ω^{-1} cm^2 mol^{-1} for 1 : 1 electrolyte in acetonitrile, confirming the covalent nature of the chloro groups [29].

Room temperature magnetic measurement of the complexes showed diamagnetism, confirming Ru^{2+}, d^6 low spin complexes.

IR spectra of $[Ru(DMSO)LCl_2]$ (L = bpp or bdmpp) showed all the absorption bands attributable to the tridentate ligands and the coordinated DMSO. One band of medium intensity at 3100 cm^{-1} and another at 2920 cm^{-1} may be assigned to $\nu_{C\text{–}H}$ aromatic of L and $\nu_{C\text{–}H}$ aliphatic of the DMSO group, respectively. Further, one absorption at 1474–1487 cm^{-1} and another at 1308–1334 cm^{-1} may be assigned to the ring stretching vibration and in plane C–H bending of the tridentate ligands [30, 31]. IR spectra of the complexes show one strong band at 1089–1102 cm^{-1} which may be assigned to $\nu_{S=O}$ of the S-bonded DMSO [32, 33]. There was no band of appreciable intensity in the region 900–1000 cm^{-1}, indicating the absence of O-bonded DMSO. The electronic absorption spectra of $[Ru(DMSO)LCl_2]$ (where L = bpp or bdmpp) show one or two absorption bands in the region 535–690 nm with € in the range 6.4×10^2 to 8.6×10^2. These bands may be assigned to d–d transition of the type ${}^1T_{1g} \leftarrow {}^1A_{1g}$ or ${}^1T_{2g} \leftarrow {}^1A_{1g}$ [34]. The molar extinction coefficient of these bands is slightly higher than the expected for d–d transitions, which may be attributed to mixing of some M → L charge transfer. One band in the region 405–430 nm with € in the range 2.5×10^3 to 4.3×10^3 was assigned to M → L type of charge transfer. Further, three more bands from 250 to 305 nm with € in the order 10^4 were observed in both complexes which may be assigned to the intra-ligand transitions of the type $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ (table 1) [12, 19].

The cyclic voltammogram of $[Ru(DMSO)(bpp)Cl_2]$ in dichloromethane using tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte has a quasi-reversible peak at $E_{1/2} = 0.37$ V ($\Delta E_p = 160$ mV), which may be due to the Ru^{III}/Ru^{II} couple. CV shows another quasi-reversible peak at $E_{1/2} = 1.0$ V ($\Delta E_p = 200$ mV), which may be assigned to Ru^{IV}/Ru^{III} couple. The cyclic voltammogram of $[Ru(DMSO)(bdmpp)Cl_2]$ also shows two quasi-reversible peaks at $E_{1/2} = 0.97$ V ($\Delta E_p = 100$ mV) and $E_{1/2} = 1.33$ V ($\Delta E_p = 220$ mV). These two redox couples could be assigned similar to its bpp analogue to Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples (figure 2) [35, 36].

${}^1H$ NMR spectrum of $[Ru(DMSO)(bpp)Cl_2]$ in DMSO-d_6 showed one singlet at δ 3.46, assigned to S-bonded DMSO [32]. Signals for coordinated bpp are observed at δ 6.63 to δ 9.26, shifted to low field compared to free bpp [27]. Signal at δ 6.63(dd) is assigned to the 4′,4″ protons, whereas signal at δ 9.26(dd) is assigned to the 5′,5″

Table 1. ${}^1H$ NMR and UV-Vis spectral data of ruthenium(II) and palladium(II) complexes.

Complex	${}^1H$-NMR (ppm)	UV-Vis (λ_{max} nm(€))
$[Ru(DMSO)(bpp)Cl_2]^a$	3.46(s), 6.63(dd), 8.26(s), 8.31(s), 8.34(s), 8.37(s), 8.42(s), 8.44(s), 9.26(dd)	535(8.6×10^2), 428(4.3×10^3), 303(2.9×10^4), 273(2.9×10^4), 265(2.6×10^4)
$[Ru(DMSO)(bdmpp)Cl_2]^b$	2.30(s), 2.59(s), 3.45(s), 6.01(s), 7.68(d), 7.98(t)	689(6.4×10^2), 595(6.9×10^2), 406(2.5×10^3), 302(3.1×10^4), 271(3.6×10^4), 249(4.8×10^4)
$[Pd(bpp)Cl]Cl^a$	6.63(dd), 7.78(s), 8.12(s), 8.20(s), 8.70(s), 8.92(s), 9.27(dd)	404(8.3×10^2), 304(3.1×10^4), 275(3.2×10^4)
$[Pd(bdmpp)Cl]Cl^a$	2.55(s), 6.54(s), 7.77(d), 8.41(t)	400(sh)(4.8×10^2), 303(3.5×10^4), 272(3.8×10^4)

UV-Vis: Electronic spectra taken in DMSO solution; ${}^1H$ NMR: ^{a} = in DMSO-d_6, ^{b} = in $CDCl_3$.

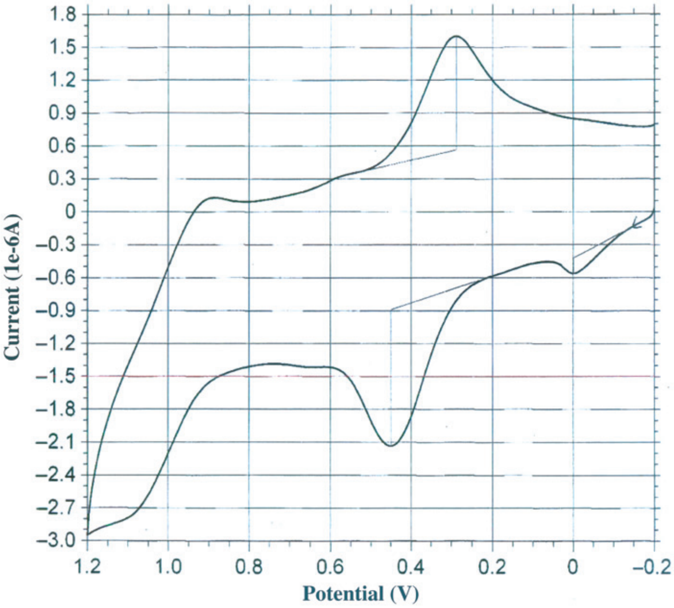

Figure 2. Cyclic voltammogram of [Ru(DMSO)(bpp)Cl_2] at 0.05 V s^{-1} at room temperature using TBAP as the supporting electrolyte.

protons of the pyrazolyl. There are five more singlets in the region δ 8.26 to δ 8.44. Two may be assigned to the 3′,3″ protons of the pyrazole and the remaining three to the 3-H, 4-H, and 5-H protons of pyridine. These assignments are similar to those reported [18], except that there are more signals, namely, one for each of these protons, which may be explained if *cis*-geometry is proposed for the complex. ^{1}H NMR spectrum of [Ru(DMSO)(bdmpp)Cl_2] in $CDCl_3$ showed singlets at δ 2.30 and δ 2.59 assigned to methyl protons of bdmpp [27], whereas a singlet at δ 3.45 is assigned to S-bonded DMSO [32]. A singlet at δ 6.01 may be assigned to 4′,4″ protons of the pyrazolyl ring and a doublet at δ 7.68 and a triplet at δ 7.98 to the 3-H, 5-H, and 4-H protons, respectively, of pyridine (table 1). From ^{1}H NMR data, a geometry with two chloro groups *trans* and bdmpp ligand and S-bonded DMSO in planar position is proposed [18].

3.2. *Palladium(II) complexes with 2,6-bis(pyrazol-1-yl)pyridine (bpp) or 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (bdmpp)*

Reactions of $PdCl_2$ with bpp or bdmpp in acetonitrile resulted in the formation of [PdLCl]Cl. Microanalytical data of the complexes are in conformity with the composition. These compounds are insoluble in common organic solvents but soluble in DMSO or DMF. Conductivity measurements in millimolar DMSO show molar conductance of 20–23 Ω^{-1} cm^2 mol^{-1}, lower than for 1 : 1 electrolyte in DMSO [29]. It seems [Pd(L)Cl]Cl (where L = bpp or bdmpp) are not completely ionized in DMSO, hence Λ_M values are somewhat lower than the expected value for 1 : 1 electrolyte.

IR spectra of [Pd(L)Cl]Cl (where L = bpp or bdmpp) show characteristic absorptions for the tridentate ligands. The shifts in the positions are similar to those described for the Ru(II) complexes. Spectra in the far IR region showed bands at 425–450 cm^{-1} and 330–350 cm^{-1}, assignable to $\nu_{\mathrm{Pd-N}}$ and $\nu_{\mathrm{Pd-Cl}}$, respectively [37]. The electronic absorption spectra of the complexes showed one broad band or a shoulder around 400 nm with € in the range of 400–830, assigned to the d–d transition of the type $\mathrm{d}_{xy} \rightarrow \mathrm{d}_{x^2-y^2}$ or d_{xz}, $\mathrm{d}_{yz} \rightarrow \mathrm{d}_{x^2-y^2}$ [30]. There are two absorptions in the region 300–250 nm (€ $\approx 10^4$) which could be assigned to intraligand transitions of bpp or bdmpp as in the case of Ru(II) complexes (*vide infra*) (table 1).

^{1}H NMR spectrum of [Pd(bpp)Cl]Cl in DMSO-d_6 showed signals at δ 6.63(dd) and δ 9.27(dd) assigned to the 4′,4″ and 5′,5″ protons of the pyrazolyl ring. Further, five more signals in the region δ 7.78 to δ 8.92 are assigned to the two 3′,3″ protons of the pyrazolyl ring and the 3-H, 4-H, and 5-H protons of pyridine. [Pd(bdmpp)Cl]Cl shows a singlet at δ 2.55 due to the methyl protons, a singlet at δ 6.54 due to the pyrazolyl 3′,3″ protons, and a doublet at δ 7.77 and a triplet at δ 8.41 to the 3-H, 4-H, and 5-H protons of pyridine (table 1), similar to Pt(II) analogues, namely, $[\mathrm{Pt(L)Cl}]^+$ [17]. Similar Pd(II) complexes described herein are proposed to have a square planar geometry with bpp or dmbpp planar tridentate.

4. Conclusions

Complexes of ruthenium(II) and palladium(II) with 2,6-bis(pyrazol-1-yl)pyridine (bpp) and 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (bdmpp) have been synthesized, $[\mathrm{Ru(DMSO)LCl_2}]$ and [PdLCl] (where L = bpp or bdmpp). Their structures have been proposed to be distorted octahedral and square planar, respectively, on the basis of various physical measurements.

Acknowledgments

Thanks are due to the Department of Science & Technology, New Delhi, for their financial support through FIST program to the department. Thanks are also due to the UGC, New Delhi, for financial support by the way of SAP-DSA, to the department.

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