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Published in:
Dalton Transactions

DOI:
10.1039/c1dt10960j

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2011

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Reinvestigating 2,5-di(pyridine-2-yl)pyrazine ruthenium complexes: selective deuteriation and Raman spectroscopy as tools to probe ground and excited-state electronic structure in homo- and heterobimetallic complexes

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Synthesis and Characterisation of 2,5-dpp and d_{10p}-2,5-dpp

2,5-di(pyridin-2-yl)pyrazine \(^{1}\)H NMR (CDCl\(_3\)): \(\delta\) 9.59 (s, 2H, 3-H, 6-H), 8.68 (d, 2H, J = 4.7 Hz, 9-H, 15-H), 8.38 (d, 2H, J = 7.8 Hz, 12-H, 18-H), 7.91 (t, 2H, J = 7.6 Hz, 11-H, 17-H), 7.80 (t, 2H, J = 5.0 Hz, 10-H, 16-H).

(d_{10p}-2,5-di(pyridin-2-yl)pyrazine) Sodium (460 mg, 0.01 mmol) was added slowly to 20 cm\(^3\) of D\(_2\)O cooled with an ice bath. 2,5-di(pyridin-2-yl)pyrazine (150 mg, 0.64 mmol) was added and heated under pressure for 6 days in a teflon lined steel dissolution bomb. The mixture was subsequently cooled to r.t. and neutralized with aqueous HCl. The aqueous phase was extracted with dichloromethane and the combined organic phases were dried over magnesium sulphate. Evaporation of the solvent yielded the deuteriated product as a white solid (0.066 g, 42%). The degree of deuteriation was determined by \(^{1}\)H NMR spectroscopy to be >98%. Yield 66 mg. \(^{1}\)H NMR (CDCl\(_3\)): \(\delta\) = 9.59 (s, 3-H, 6-H), 8.68 (s, 2H, 9, 15), 8.38 (s, 2H, 12, 18), 7.80 (s, 2H, 11, 17), 7.73 (s, 2H, 10, 16).

Synthesis of mononuclear ruthenium(II) complexes 1a-d

2,5-di(pyridin-2-yl)pyrazine (0.21 mmol) were dissolved in 5 cm\(^3\) of an ethanol/water (3:1 v/v) and heated at reflux. Subsequently, [Ru(2,2'-bipyridine)\(_2\)] \(\text{H}_2\)O (0.14 mmol) dissolved in 20 cm\(^3\) of an ethanol/water mixture was added slowly over a period of 1 h. The brown solution was heated at reflux for 6 h. After cooling to r.t. ethanol was removed in vacuo and non-reacted starting material was removed by filtration. 2 cm\(^3\) of saturated NH\(_4\)PF\(_6\)(aq) was added to the filtrate, yielding a brown precipitate. The crude product was collected and washed with small amounts of water and diethyl ether. Recrystallization from acetone/water (2:1 v/v) afforded brown crystalline solids.

[bis-(2,2'-bipyridine)-(2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)] \((\text{PF}_6)_2\) \(\text{H}_2\)O (1a)

Yield 71%. \(^{1}\)H NMR (DMSO-\(d_6\)): \(\delta\) = 10.04 (s, 1H, 3-H), 9.04 (d, 1H, 12-H), 8.90-8.51 (m, 4H, bipy), 8.59 (s, 1H, 6-H), 8.53 (d, 1H, 15-H), 8.42 (d, 1H, 18-H), 8.28-8.19 (m, 5H, bipy, 11-H), 8.08 (d, 1H, bipy), 8.03 (t, 1H, 17-H), 7.83 (d, 1H, bipy), 7.80 (d, 1H, 9-H), 7.74 (s, 2H, bipy), 7.67-7.57 (m, 4H, bipy, 10-H), 7.52 (m, 1H, 16-H), 7.48 (m, 1H, bipy). \(C_{34}H_{26}F_{12}N_{8}P_{2}Ru.H_2O\) (955.64): calcd. C 42.73, H 2.95, N 11.73; found C 42.14, H 2.94, N 11.63.

[bis-(2,2'-bipyridine)-(2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)] \((\text{PF}_6)_3\) \(\text{H}_2\)O (1b)

Yield 48%. \(^{1}\)H NMR (DMSO-\(d_6\)): \(\delta\) = 10.04 (s, 1H, 3-H), 9.04 (d, 1H, 12-H), 8.90 (s, 4H, bipy), 8.89 (s, bipy), 8.86 (s, bipy), 8.85 (s, bipy), 8.59 (s, 1H, 6-H), 8.53 (d, 1H, 15-H), 8.42 (d, 1H, 18-H), 8.28 (s, bipy), 8.25 (d, 1H, 17-H), 8.23 (s, bipy), 8.20 (s, bipy), 8.19 (s, bipy), 8.08 (s, bipy), 8.03 (t, 1H, 17-H), 7.83 (s, bipy), 7.80 (d, 1H, 9-H), 7.74 (s, bipy), 7.72 (s, bipy), 7.63 (s, bipy), 7.60 (t, 1H, 10-H), 7.59 (s, bipy), 7.57 (s, bipy), 7.52 (t, 1H, 16-H), 7.48 (s, bipy). \(C_{34}H_{26}D_{10}F_{12}N_{8}P_{2}Ru.H_2O\) (971.74): calcd. C 42.02, H 2.90, N 11.53; found C 42.14, H 2.94, N 11.63.

[bis-(2,2'-bipyridine)-(2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)]\((\text{PF}_6)_4\) \(\text{H}_2\)O (1c)

Yield 67%. \(^{1}\)H NMR (DMSO-\(d_6\)): \(\delta\) = 10.04 (s, 3-H), 9.04 (s, 12-H), 8.90-8.85 (m, 4H, bipy), 8.59 (s, 6-H), 8.53 (s, 15-H), 8.42 (s, 18-H), 8.28-8.19 (m, 4H, bipy, 11-H), 8.08 (d, 1H, bipy), 8.03 (s, 17-H), 7.83 (d, 1H, bipy), 7.80 (s, 9-H), 7.72 (d, 2H, bipy), 7.63-7.57 (m, 3H, bipy, 10-H), 7.52 (s, 16-H), 7.48 (t, 1H, bipy). \(C_{34}H_{26}D_{10}F_{12}N_{8}P_{2}Ru.H_2O\) (965.70): calcd. C 42.29, H 2.9, N 11.6; found C 42.33, H 3.05, N 11.41.

[bis-(2,2'-bipyridine)-(d_{10p}-2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)]\((\text{PF}_6)_2\) \(\text{H}_2\)O (1d)

Yield 61%. \(C_{34}D_{10}F_{12}N_{8}P_{2}Ru.H_2O\) (981.80): calcd. C 41.59, H 2.88, N 11.41; found C 41.83, H 2.82, N 11.29.

Synthesis of dinuclear ruthenium(II) complexes 2a-d.
2.5-di(pyridin-2-yl)pyrazine (0.21 mmol) and [Ru(2,2'-bipyridine)Cl₂]_2H₂O (0.47 mmol) were dissolved in 20 cm³ of ethanol/water (3:1 v/v) and heated at reflux for 6 h. After cooling to r.t. ethanol was removed in vacuo and non-reacted starting material was removed by filtration. 2 cm² of saturated NH₄PF₆ solution were added to the filtrate, yielding a dark precipitate. The crude precipitate was collected and washed with small amounts of water and diethyl ether. Recrystallization from acetone/water (2:1 v/v) afforded dark crystalline solids. The complexes are obtained as diastereomeric mixtures (ÂΛ and ÂΛ/Â∆ isomers).

\[
[\mu-(2,5-di(pyridin-2-yl)pyrazine)bis-(bis-2,2'-bipyridine) ruthenium(II)]\left[PF_6\right]_4(CH_2)CO (2a)
\]
Yield 69%. ¹H NMR (DMSO-D₆): δ = 8.91-8.80 (m, 8H, bipy), 8.68 (s, 1H, dpp), 8.59 (s, 1H, dpp), 8.33-8.11 (m, 11H, dpp, bipy), 8.05-8.02 (m, 2H, dpp, bipy), 7.81-7.80 (m, 2H, dpp), 7.77-7.71 (m, 2H, bipy), 7.68-7.64 (m, 2H, bipy), 7.50-7.44 (m, 4H, bpy).

\[
[\mu-(2,5-di(pyridin-2-yl)pyrazine)bis-(bis-2,2'-bipyridine) ruthenium(II)]\left[PF_6\right]_4(CH_2)CO (2b)
\]
Yield 75%. ¹H NMR (DMSO-D₆): δ = 8.68 (s, 1H, dpp), 8.61 (s, 1H, dpp), 8.18-8.11 (m, 2H, dpp, bipy), 7.77-7.71 (m, 2H, dpp), 7.61-7.56 (m, 2H, dpp). C₆H₂D₅N₁P$_{10}$Ru$_{10}$.(CH₂)₄CO (1699.07): calcd. C 39.63, H 2.89, N 9.73; found C 39.39, H 3.21, N 10.04.

\[
[\mu-(d_{30}-2,5-di(pyridin-2-yl)pyrazine)bis-(bis-2,2'-bipyridine) ruthenium(II)]\left[PF_6\right]_4(CH_2)CO.H₂O (2c)
\]
Yield 32%. ¹H NMR (DMSO-D₆): δ = 8.91-8.80 (m, 8H, bipy), 8.33-8.20 (m, 8H, bipy), 8.05-8.02 (m, 2H, bipy), 7.68-7.64 (m, 2H, bipy), 7.62-7.50 (m, 6H, bipy), 7.47-7.43 (m, 2H, bipy), 7.30-7.27 (m, 2H, bipy). C₆H₁₂D₅F₃N₁P$_{10}$Ru$_{10}$.0.5(CH₂)₄CO.H₂O (1727.14): calcd. C 39.63, H 2.89, N 9.73; found C 39.39, H 3.21, N 10.04.

\[
[\mu-(d_{30}-2,5-di(pyridin-2-yl)pyrazine)bis-(bis-2,2'-bipyridine) ruthenium(II)]\left[PF_6\right]_4(CH_2)CO • 2 H₂O (2d)
\]
Yield 75%. ¹H NMR (DMSO-D₆): no signals. C₆H₁₂D₅F₃N₁P$_{10}$Ru$_{10}$.2(CH₂)₄CO.2H₂O (1777.35): calcd. C 38.52, H 2.93, N 9.46; found C 38.82, H 3.29, N 9.88.

[Ruthenium(II)(2,2'-bipyridine)$_2$µ-2,5-di(pyridin-2-yl)pyrazine]PdCl₂] (PF₆)₂ 2 H₂O (3)

Ia (0.100 mg, 0.10 mmol) was dissolved in 5 ml of dichloromethane and added drop wise to a solution of [Pd(acetonitrile)Cl₂] (0.026 g, 0.10 mmol) in 5 ml of dichloromethane. The reaction mixture was heated at reflux for 24 h. Subsequently, the mixture was cooled to room temperature and the product was precipitated by addition of 10 ml of n-hexane. After filtration and washing with 10 ml of diethyl ether a reddish purple solid was obtained. Yield: 0.107 g (0.09 mmol, 90%). Anal. Calcd for C₆H₁₂D₅F₃N₁P$_{10}$Ru$_{10}$.PdRu • 2 H₂O (1150.98): C, 35.48; H, 2.63; N, 9.74%. Found: C, 35.30; H, 2.22; N, 9.31%. ¹H-NMR (Acetonitrile-d₆, 400MHz): δ = 10.05 (s, 1H, 3-H), 8.91 (d, J = 4.8 Hz, 1H, 15-H), 8.62 (d, J = 8.4 Hz, 1H, 12-H), 8.57 – 8.52 (m, 4H, bppy), 8.42 (s, 1H, 6-H), 8.15 (dd, J = 6.0 Hz, J = 1.8 Hz, 1H, 11-H), 8.19-8.08 (m, 4H, bppy), 8.10 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H, 17-H), 7.81 (d, J = 8.0 Hz, 1H, 9-H), 7.82-7.75 (m, 4H, bppy), 7.66 (d, J = 7.6 Hz, 1H, 18-H), 7.59 (m, 1H, 10-H), 7.61 (m, 1H, 16-H), 7.50-7.44 (m, 4H, bppy).

[Ruthenium(II)(2,2'-bipyridine)$_2$µ-2,5-di(pyridin-2-yl)pyrazine]PtCl₂] (PF₆)₂ 2 H₂O (4)

Ia (0.100 mg, 0.10 mmol) was dissolved in 5 ml of dichloromethane and added drop wise to a solution of [Pt(DMSO)Cl₂] (0.042 g, 0.10 mmol) in 5 ml of dichloromethane. The reaction mixture was heated at reflux for 24 h. The mixture was allowed to cool to room temperature and the product precipitated by addition of 10 ml of n-hexane. After filtration and washing with 10 ml of diethyl ether a reddish purple solid was obtained. Yield: 0.115 g (0.09 mmol, 90%). Anal. Calcd for C₆H₁₂D₅F₃N₁P$_{10}$PtRu • 2 H₂O (1239.64): C, 32.94; H, 2.44; N, 9.04%. Found: C, 32.93; H, 2.07; N, 8.96%. ¹H-NMR (Acetonitrile-d₆, 400MHz): δ = 10.48 (s, 1H, 3-H), 9.46 (d, J = 4.8 Hz, 1H, 15-H), 8.63 (d, J = 8.4 Hz, 1H, 12-H), 8.57 – 8.48 (m, 4H, bppy), 8.55 (d, J = 8.0 Hz, 1H, 18-H), 8.32 (s, 1H, 6-H), 8.19-8.05 (m, 4H, bppy), 8.19 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, 11-H), 8.07-7.55 (m, 4H, bppy), 8.05 (dd, J = 8.0 Hz, J = 1.8 Hz, 1H, 17-H), 7.81 (d, J = 5.6 Hz, 1H, 9-H), 7.67-7.42 (m, 4H, bppy), 7.48 (m, 1H, 10-H), 7.42 (m, 1H, 16-H).
Fig. S1 rR spectra of 1a at $\lambda_{exc}$ (a) 785 nm (SERS) and (b) 450 nm and (c) 355 nm in CH$_3$CN (solvent subtracted)

Fig. S2 UV/Vis absorption spectra of a) 1a, b) 2a, c) 3 and d) 4 in CH$_3$CN