Cis- & trans-isomerism in \([\text{Cl}_2\text{Ru(dppb)}\text{N-N}]\) complexes: Synthesis, structural characterization and X-ray crystal structure of dichloromethane solvated cis-diaminebis(diphenylphosphinobutane)-ruthenium(II) complex

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HIGHLIGHTS

- Synthesis of cis & trans isomer of \([\text{RuCl}_2(\text{dppb})(\text{N-N})]\) complexes.
- Crystal structure of cis- \([\text{RuCl}_2(\text{dppb})(\text{N-N})]\) isomer.
- cis & trans isomerization is supported by \(^{31}\text{P}\) NMR.

GRAPHICAL ABSTRACT

ABSTRACT

Three diamine-bis(diphenylphosphinobutane)ruthenium(II) complexes, isolated from the reaction of \([\text{Cl}_2\text{Ru(dppb)}]\) with diamines viz., 2,2-dimethyl-1,3-diaminopropane, 1,2-diaminocyclohexane and 1,8-diaminonaphthalene are reported. The synthesized complexes have been characterized on the basis of various physico-chemical studies viz., EDX, IR, FAB-MS, UV/Vis, NMR, TG-DTG and EXAFS studies. \(^{31}\text{P}\) NMR investigations confirm that the complex 3 is in cis form while the complexes 1–2 appear in trans form. The structure of complex 3 has been additionally determined by single crystal X-ray diffraction showing solvated dichloromethane. Furthermore, complex 3 crystallizes as monoclinic unit cell with \(P2(1)/n\) space group.

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Introduction

Phosphine ligands have been intensively used in coordination chemistry because of their electron donating properties \([1–4]\). Among them, diphosphines have received much attention due to their tendency to form more stable complexes than their non
chelating phosphine analogs under the harsh reaction conditions required for catalysis [5–9]. In the last few years, lot of work has been reported on the dynamic behavior of transition metal complexes containing monodentate and bidentate ligands, and it still remains an active area of research interest [10,11]. In recent years, the chemistry of Ru(II) complexes possessing a chelating diphosphine (P-P) and diamine (N-N) ligands has been a topic of great interest, and represent an attractive class of compounds on account of their various catalytic and bioinorganic chemistry applications [3,11–16]. Furthermore, Noyori discovered that [RuCl2(diphosphine)2(diamine)2] complex can catalyze the hydrogenation of unfunctionalized ketones showing chemoselectivity on C=O bond over the more reactive C≡O bond through a favored pericyclic transition state [11]. Moreover, the chelate diphosphine ligands decreased the number of isomers compared to monodentate phosphine ligands, which de-complicated the structural identification of synthesized complexes [17]. Therefore, in continuation of our ongoing interest in chemistry of various diamines diphos- phineruthenium(II) complexes and their applications [17–20], herein, we have reported the synthesis of diamine[bis(diphenylphosphino)butane] ruthenium(II) complexes of general formula [RuCl2(dppb)(N-N)], obtained from the reaction of 1,4-bis(diphenylphosphino)butane with various diamines viz., 2,2-dimethyl-1, 3-diaminopropane, 1,2-diaminocyclohexane and 1,8-diaminonaphthalene, and finally we got cis- and trans-[RuCl2(dppb)(N-N)] isomer complexes. The thermodynamically favoured isomer, cis-RuCl2(dppb)(N-N)] with 2,2-dimethyl-1,3-propanediamine as diamine co-ligand, was confirmed by single crystal X-ray measurements.

**Experimental**

**Materials, and instrumentations**

All reactions were carried out in argon atmosphere by using standard high vacuum and Schlenk-line techniques. 1,4-bis(diphenylphosphino)butane (dppb), [RuCl2{(Ph2P)3}], 1,2-diaminocyclohexane, 2,2-dimethyl-1,3-diaminopropane and 1,8-diaminonaphthalene were available from Merck and used as received. Elemental analyses were carried out on Elementar Varrio EL analyzer. High-resolution (1H), 13C[1H], and 31P[1H] NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. FT-IR and FAB-MS spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. FT-IR vs. scans. The non-hydrogen atoms were refined anisotropically and FAB-MS; (m/z) 756.1 [M]+. Anal. Found: C, 60.42; H, 5.08; N, 3.70; Cl, 9.37. 62%; UV–Vis CHCl3 210, 250, 280, 510 nm.

1. [RuCl2{(Ph2P)3}][RuCl2(dppb)] precursor (0.1 g) was treated with the naphthalene-1,8-diamine ligand (0.06 g, 0.08 mmol), Yield (85%), yellow crystal, m.p. (decomp.), 355 °C. IR (KBr, ν cm−1): 3360, 3140, 2870 and 314 cm−1, assigned to −NH2, Ph−CH, alkyl−CH and Ru−Cl, respectively. 1H NMR (CDCl3): δ (ppm) 1.58 (m, 4H, PCH2), 2.62 (m, 4H, PCH2), 2.98 (b, 4H, NH2), 7.00–7.80 (3 m, 26H, C6H5), 31P[1H](CDCl3): δ (ppm) for trans δ (ppm) 48.2. 13C[1H]NMR (CDCl3): δ (ppm) 23.90 (s, PCH2), 26.70 (m, PCH2), 129.00–138.00 (8s, Ph), FAB-MS; (m/z) 756.1 [M]+. Anal. Found: C, 60.42; H, 5.08; N, 3.70; Cl, 9.37. 62%; UV–Vis CHCl3 210, 250, 280, 510 nm.

2. [RuCl2{(Ph2P)3}][(dppb)] precursor (0.1 g) was treated with the 2-cyclohexane-1,2-diamine ligand (0.05 g, 0.07 mmol). Yield (90%), yellow–brown powder, m.p. 314 °C (dec.). 1H NMR (CDCl3): δ (ppm) 0.88–2.14 (m, 10H, C6H10), 1.81 (m, 2H, CH2), 2.49–2.81 (m, 8H, PCH2, PCH2, CH2, NH2), 7.12–7.66 (2 m, 20H, C6H5). 31P[1H] NMR (CDCl3): δ (ppm) 46.23. 13C[1H] NMR (CDCl3): δ (ppm) 19.31 (s, CH2), 24.96 (s, CH2CH2CH2), 26.15 (m, PCH2), 36.39 (s, NCH2CH2), 57.62 (s, NCH2CH2), 128.16 (m, m-C6H5), 129.15 (m, p-C6H5), 133.11 (m, o–C6H5). FAB-MS; (m/z) 712.1 [M]+. Anal. Found: C, 57.48; H, 5.86; Cl, 10.10F; 4.07. Calc. for C35H34Cl2N2P2Ru: C, 57.30; H, 5.94; Cl, 9.55; N, 3.93%, UV–Vis CHCl3 240, 280, 510 nm.

3. [RuCl2{(Ph2P)3}][(dppb)] precursor (0.1 g) was treated with the 2,2-cyclohexane-1,3-propanediamine ligand (0.02 g, 0.07 mmol). Yield (85%), yellow crystal, m.p. 272 °C (decomp.). IR (KBr, ν cm−1): 3380–3270, 3180, 2900–2800 and 270–285 cm−1, assigned to −NH2, Ph−CH, alkyl−CH and Ru−Cl, respectively. 1H NMR (CDCl3): δ (ppm) 0.83 (s, 6H, CH3), 1.48 (m, 4H, PCH2CH2), 2.54 (m, 4H, PCH2), 2.78, 2.80 (b, 8H, CH2N, NH2), 7.20–7.70 (2 m, 20H, C6H5). 31P[1H](CDCl3): δ (ppm) (AX pattern with δA = 45.0 and δX = 54.7 ppm, coupling constant of P–P atoms, JXX = 48.8 Hz). 13C[1H]NMR (CDCl3): (ppm) 22.70 (s, PCH2), 25.13 (s, CH3), 26.03 (m, PCH2), 49.92 (s, NCH2CH2), 128.13 (m, m-C6H5), 128.96 (s, p-C6H5), 132.93 (m, o–C6H5), 136.59 (m, o–C6H5), FAB-MS; (m/z) 700.1 [M]+. Anal. Found: C, 56.46; H, 6.17; N, 3.97; Cl, 10.24. Calc. for C33H34ClN2P2Ru: C, 56.57; H, 6.04; N; 4.00; Cl, 10.12%, UV–Vis CH2Cl2: 325, 495 nm.

**Synthesis of diamine[bis(diphenylphosphino)butane]ruthenium(II)-complexes (1–3)**

The precursor compound [RuCl2{(Ph2P)3}] and dppb in dichloromethane in argon atmosphere. The precursor compound, [RuCl2{(Ph2P)3}], on treatment with corresponding diamines (10% excess) viz., 1,8-diaminonaphthalene, 1,2-diaminocyclohexane and 2,2-dimethyl-1,3-diaminopropane in equimolar ratio in dichloromethane leads to the color change in reaction from green to yellow. The volume of colored solution was concentrated to 1 ml under reduced pressure followed by the addition of 30 ml of diethyl ether to cause precipitation. The obtained precipitate was isolated and re-crystallized in dichloromethane–n-hexane mixture to obtain analytically pure compound. Crystals suitable for X-ray measurement were obtained for complex 3. No crystal was found suitable for X-ray measurement for complexes 1 and 2.

**X-ray structural analyses**

All measurements were performed on o/θ/ω-scan technique on CAD4 (Nonius) automatic diffractometer, with graphite monochro- matized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The control of the intensity without appreciable decay (1.2%) yielded 9022 unique reflections, of which 10558 exhibited I > 2σ(I). After Lorenz and polarization corrections, the absorption corrections were applied using ψ-scans. The non-hydrogen atoms were refined anisotropically by the full-matrix least-square techniques using the program SHELXL97 [21]. All of the hydrogen atoms bonded to C atoms were geometrically located and treated using a riding model, with C−H = 0.93–0.97 Å and Uiso(H) = 1.2 or 1.5Ueq(C).

**Results and discussion**

Earlier, we reported ruthenium complexes of diphenylphosphino- butane, dppb with three different diamine co-ligands viz., 1,3-diaminopropane, 2-methyl-1,2-ethanediamine, and 1,4-diaminobutane, and we isolated single crystal of ruthenium complex with 1,3-diaminopropane as trans-Cl2Ru-isomer without solvent. Unfortunately, we could not find suitable crystal structure of the remaining complexes [17]. Furthermore, in the synthesis of [RuCl2(H2(C6H4P2H2))2(diamine)] complexes, we used
diphosphine as 1,3-diphosphine ligand with C=C function group (H₂C=C(CH₂PPh₂)), and that was complete different system [18].

Herein this article, reported mixed ligand cis/trans complexes were obtained by the reaction of [RuCl₂(PPh₃)₂(dppe)] with excess amount of the entirely different diamines viz., 1,2-diaminocyclohexane, 2,2-dimethyl-1,3-diaminopropane and 1,8-diaminonaphthalene (Scheme 1) in dichloromethane. Different bidentate diamine used as co-ligands in complex synthesis were used to stabilize both cis and trans-[Cl₂Ru(dppb)(N-N)] isomer complexes. All the desired complexes were characterized on the basis of elemental analyses, EDX, IR, FAB-MS, UV/Vis, NMR, TG-DTG and EXAFS studies. Additionally, one of the complex with 2,2-dimethyl-1,3-diaminopropane was determined by single crystal X-ray diffraction showing complex exists as cis-Cl₂Ru-isomer with one molecule of dichloromethane. Unfortunately, we could not find other crystals suitable for single crystal X-ray diffraction. Furthermore, we introduced EXAF in the current work as a power tool to confirm the coordination number while we did not use it in our previous work.

**EDX analysis**

Formation of complexes was confirmed by EDX measurements indicating the number of signals coming from Ru, P, Cl, N and C atoms are consistent with the proposed molecular formula of the complexes [Fig. 1S].

**Mass spectra**

The FAB-MS molecular ion peak(s) \([M^+] m/z\) observed at 756.1, 712.1 and 700.1 were consistent with the proposed molecular formulae of their respective complexes 1, 2 and 3, respectively. The FAB-MS spectrum of complex 3 showed a molecular ion peak of \([M^+] m/z = 700.1\), corresponding to the molecular formula of its parent ion \([C₃₃H₄₂Cl₂N₂P₂Ru]^+\) at 100% of the base peak intensity. The main first three fragments that appeared in the spectrum correspond to \([M^+] m/z = 664.1 \ [C₃₃H₄₁ClN₂P₂Ru]^+, 40%, ([M^+]·HCl), and 628.2 \ [C₃₃H₄₀N₂P₂Ru]^+ 20%, ([M^+]·Cl₂) [Fig. 2S].

**IR spectral investigations**

Preliminary identification of the synthesized complexes has been obtained from IR spectra which revealed four main sets of characteristic absorptions in the ranges of 3380–3270, 3180, 2900–2800 and 270–285 cm⁻¹, assigned to A₂NH₂, A₂CH, alkyl–CH and Ru–Cl stretching vibrations, respectively. All other function group vibrations appeared at their expected positions [Fig. 3S].

**Electronic absorption spectral**

The electronic absorption spectra of the reported complexes, recorded in dichloromethane at room temperature, showed intense transitions in the UV/Vis region. The UV bands observed at 200–300 nm range have been assigned to intra-ligand \(\pi–\pi^*/\eta–\pi^*\) transitions [22,23], while the bands observed at \(≈510\) nm have been tentatively assigned to M–L charge transfer transitions (MLCT) [Fig. 4S] [24].

**EXAFS measurement**

EXAFS of complex 1 was carried out to support structural formula of the synthesized complex as well as to determine the bond lengths between the Ruthenium center and the coordinating P, N,
and Cl atoms of the ligands. The k^3 weighted EXAFS function of complex can be described by six different atom shells. For the most intense peak of the Fourier Transform, two equivalent phosphorus, two nitrogen atoms and two chlorine atoms with Ru–P, Ru–N and Ru–Cl bond distances of 2.27, 2.18 and 2.42 Å, respectively, are reported [Fig. 1].

NMR investigation

Structure of the reported complexes was further supported by ^1H, ^31Cl[^1H] NMR and ^31P[^1H] NMR spectroscopic studies. The ^1H NMR spectra Ru(II) complexes have been recorded in CDCl₃, and their assignments are given in experimental part. Several characteristic sets of signals attributed to the dppb and diamine ligands are observed. The integration of the ^1H resonances confirm that dppb and diamine ratio is in agreement with the structural composition of cis- and trans-[Cl₂Ru(dppb)(N-N)] complexes. ^31P NMR spectra revealed the formation of the kinetic favoured trans-isomer with equivalent number of phosphorus atoms (P trans to N) singlet 31Pδ ~ 46.2 ppm and 48.1 ppm for complex 1 and 2 at room temperature, respectively [Fig. 2a and b] [17,22–24]. The 31P NMR spectrum of complex 3 revealed two doublets indicating the formation of thermodynamically favoured cis-isomer with an equivalent number of phosphorus atoms at room temperature (AX pattern with δₐ = 45.0 and δₓ = 54.7 ppm, coupling constant of P–P atoms, Jₓₓ = 48.8 Hz) [Fig. 3c]. The 31P chemical shifts and the 31P–31P coupling constants are consistent with a cis arrangement of P atoms in dppb in complex 3. The 31P chemical shifts ~45 ppm which sited to PA belongs to P trans to N, while P trans to Cl (PX) sited to higher chemical shift ~55 ppm [18,25].

TG A/DTG studies

The TGA/DTG studies of the complexes were investigated at temperature 25–900 °C at a heating rate of 10 °C/min. The TGA/DTG graph clearly shows that there is no weight loss up to 25–295 °C, thus indicating the absence of coordinated or uncoordinated water. All the three complexes undergo one step decomposition with weight loss experimentally at 82.5%, thus showing that coordinated chlorides, diamine, dppb ligands have been de-structured at temperature 300–400 °C with exothermic DTG peaks at
in cis-[RuCl₂(dppb)(N-N)] isomeric form. The distorted octahedral geometry around the ruthenium center exists with two Ru–N distances of 2.194 Å and 2.128 Å, two Ru–Cl distances of 2.517 Å and 2.429 Å and two Ru–P distances equal to 2.271 Å and 2.286 Å. The coordination angle of the diamine chelate ring results in a distinct N–Ru–N angle of 84.5°, departing from ideal value by up to approximately 5.5°, due to six-membered ring chelating nature of dppb ligand. The P–Ru–P angle is equal to 92.2° departing from ideality due to seven-membered ring chelating nature of the dppb ligand. The dichloro Cl–Ru–Cl angle was found to be 89.43°. In the crystal structure, there are a number of RuCl₂–HN contacts smaller than 3.0 Å, indicating the presence of unconventional intra-hydrogen bonds [25].

### Conclusion

In this work, we reported the synthesis of three thermodynamically favoured isomers of general formula, [Cl₂Ru(dppb)(N-N)] +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.08.039.

### X-ray structure determination of the complex

The molecular structure of complex 3 has been determined by single crystal X-ray diffraction, and the ORTEP diagram and packing mode is given in Figs. 3 and 4, respectively. Complex crystallizes in the monoclinic space group P2₁/n. The crystal data and structure refinement is summarized in Table 1. Ruthenium center is coordinated by two bidentate ligands in crystal data and structure refinement is summarized in Table 1. The distorted octahedral coordination environment around the ruthenium centre exists with two Ru–N distances of 2.194 Å and 2.128 Å, two Ru–Cl distances of 2.517 Å and 2.429 Å and two Ru–P distances equal to 2.271 Å and 2.286 Å. The distortion angle of the diamine chelate ring results in a distinct N–Ru–N angle of 84.5°, departing from ideal value by up to approximately 5.5°, due to six-membered ring chelating nature of dppb ligand. The P–Ru–P angle is equal to 92.2° departing from ideality due to seven-membered ring chelating nature of the dppb ligand. The dichloro Cl–Ru–Cl angle was found to be 89.43°. In the crystal structure, there are a number of RuCl₂–HN contacts smaller than 3.0 Å, indicating the presence of unconventional intra-hydrogen bonds [25].

### Acknowledgments

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding of this research through the Research Group Project no. RGP-VPP-257.

### Appendix A. Supplementary material

Crystallographic data corresponding to the structural analysis have been deposited within the Cambridge Crystallographic Data Centre, CCDC No. 953474 for complex {cis-[Cl₂Ru(P-P)(N-N)]H₂CCl₃}. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.08.039.

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