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Research Article

One-Pot Efficient Synthesis of 1,4-Bis (2,2′:6′,2″-Terpyridin-4′-Yl) Benzene Ditopic Bridging Ligand

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Abstract

The ditopic bridging 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl) benzene (I) was prepared in a controlled one-pot condensation reaction of acetylpyridine, benzene-1,4-dicarbaldehyde and ammonium acetate in basic medium in EtOH in high yield. The product was characterised using conventional methods.

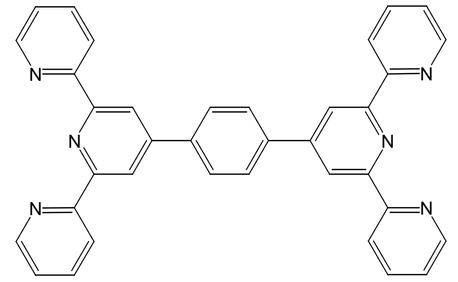
Keywords: 2,2′:6′,2″-terpyridine, Symmetrical bridging ligands, Synthesis

Introduction

In the line of part of our studies, we conducted research projects involving preparation of poly-pyridine ditopic bridging ligands for the purpose of preparation of heterodinuclear Ru (II)-Co (III) complexes [1-6] In our studies, we have been interested in the preparation of bridging ligands in which at least one binding site was based on 2,2’:6’,2”-terpyridine ligand binding domain.

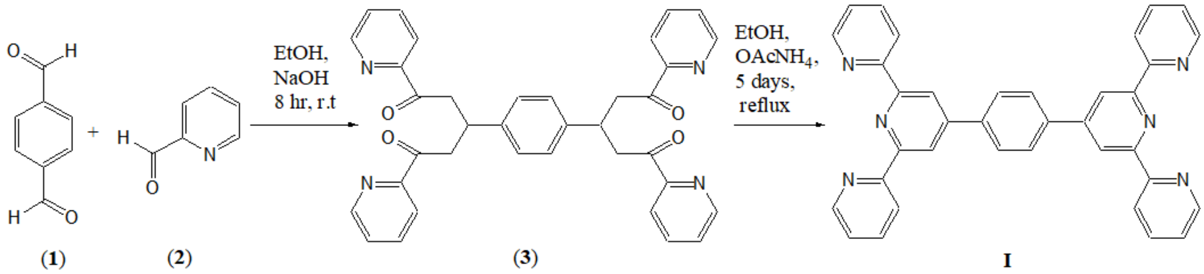
2,2’:6’,2”-terpyridine ligand was appealed at one end of the bridging ligands, because of its geometry for being planar in addition to its tridentate binding site which can bind to a transition metal ion such as ruthenium ion [7-21]. In our previous studies, we have reported preparation of terpyridine types of bridging ligands with two different binding sites, [1,4&5] because planar terpyridine binding domain ensures a meridional arrangement of the nitrogen donor atoms which leads to the reduction of the number of possible isomers when an octahedral metal coordination forms at this site. Additionally, the different binding sites within the ligands provide coordination discrimination in which different metal ions can be selectively coordinated to the appropriate site.

In this study, we took the opportunity for the preparation of symmetrical terpyridine bridging ligands for the purpose of our investigation to accomplish comparison studies with which non-symmetrical ligands were studied. To conduct our investigation, we have re-visited the preparation of a symmetrical ligand 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl) benzene (I) which was reported earlier by Constable and his group [22]. The ligand (I) is well known in the literature and available commercially. X-ray structure of the ligand was also reported [23] (I) figure.



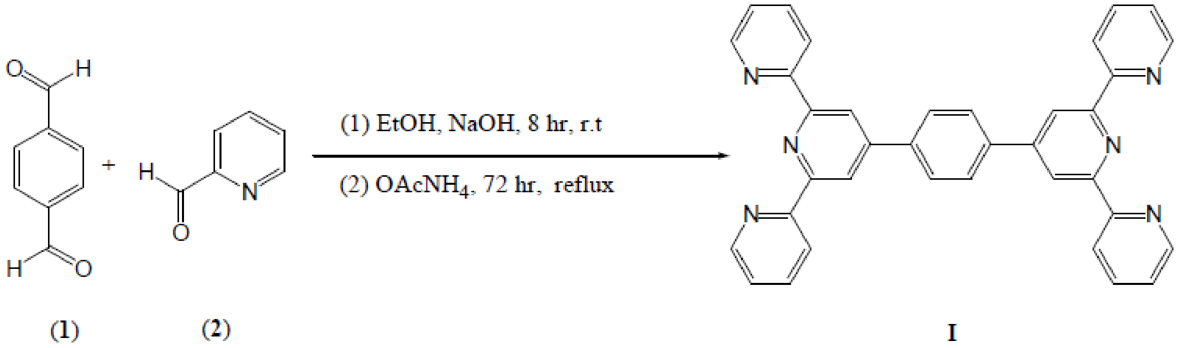
(I)

Constable, et al. reported the preparation of the ligand (I) (Scheme 1) which involved a two-step reaction of benzene-1,4-dicarbaldehyde (1) with 4.5 equivalents of 2-acetylpyridine (2) results in the formation of a tetraketone 1,4-bis[1,5-dioxo-1,5-bis(2-pyridyZ)pentan-3-yl]benzen (3) in 64% yield and the reaction of (3) with ammonium acetate in 5 days to obtain the ligand in 39% yield (Scheme 1).



Scheme 1: Two-step ynthesis of ligand 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl) benzene (I) [22].

Following the procedure reported by *Constable, et al.* [22] we found that, although the tetraketone (3) is isolable and characterisable, without separation and isolation of the compound (3), by addition of ammonium acetate to the reaction mixture and refluxing for 72 hours, the target ligand (I) can be obtained in 84% overall yield (Scheme 2).



Scheme 2: One-pot synthesis of ligand 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl) benzene (I) (this study).

To monitor the reaction progression, after about 8 hours of the reaction of (1) and (2) in basic EtOH at r.t, required amount of the white precipitate which was formed was taken, washed and dried. Characterisation of the isolated tetraketon (3) using NMR was not achieved due to poor solubility of the compound and presumably because of possible keto-enol tautomerisation on the NMR time scale which was also observed by Constable et.al in their previous studies [22, 24]. However, characterisation of compound (3) in solid state was performed using FTIR spectrophotometry and elemental analysis. The FTIR spectrum of (3) in Figure 1 shows a peak at 1700.69 cm^{-1} which can be assigned for υC=O stretching frequency as a characteristic of the non-conjugated carbonyl group. These observations were consistent to those reported earlier [22] The hydroxyl stretching mode, υO-H 3433.89 cm^{-1} is assigned for OH group in a possible occurrence of keto-enol tautomerism (Figure 1).

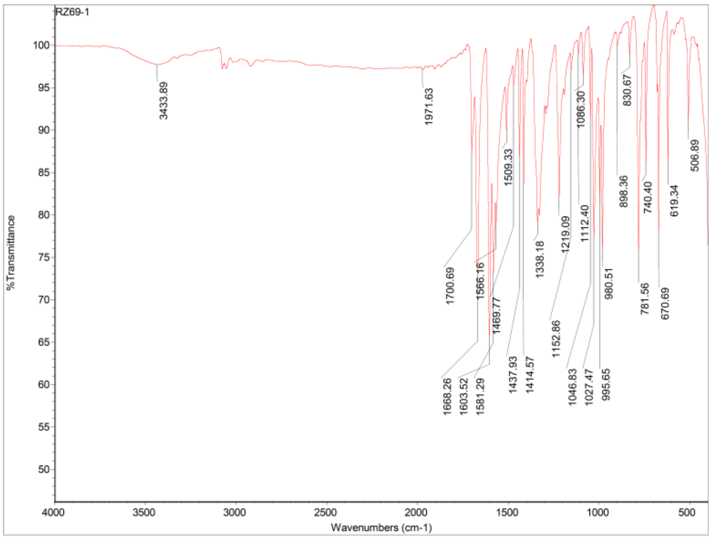


Figure 1: The FTIR (KBr) spectrum of [3].

Colour change was observed upon addition of ammonium acetate to the reaction mixture. The mixture was allowed to reflux for 72 hours during which time an off-white solid was precipitated in a dark solution. The precipitate was separated by filtration, washed with EtOH and air-dried to afford ligand (I) in 84% yield. The product which was obtained was fully characterised using NMR, Mass, IR and elemental analysis (Figures 2-4). All data were consistent to those reported by Constable and his research group [22] (Figure 2-4).

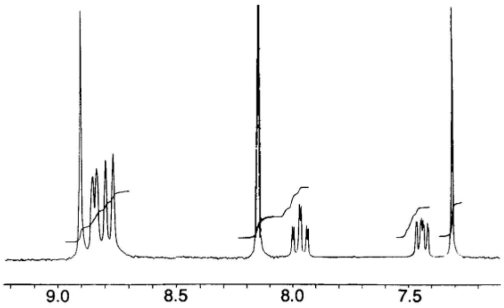


Figure 2: The 1H NMR spectrum of (I) in CDCl3 (400 Mhz).

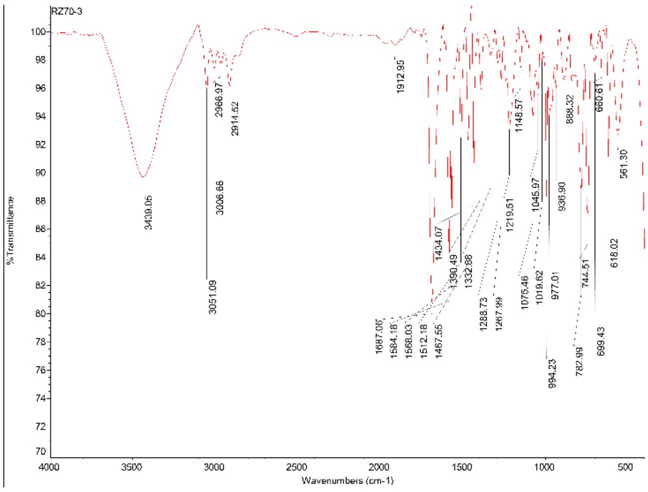
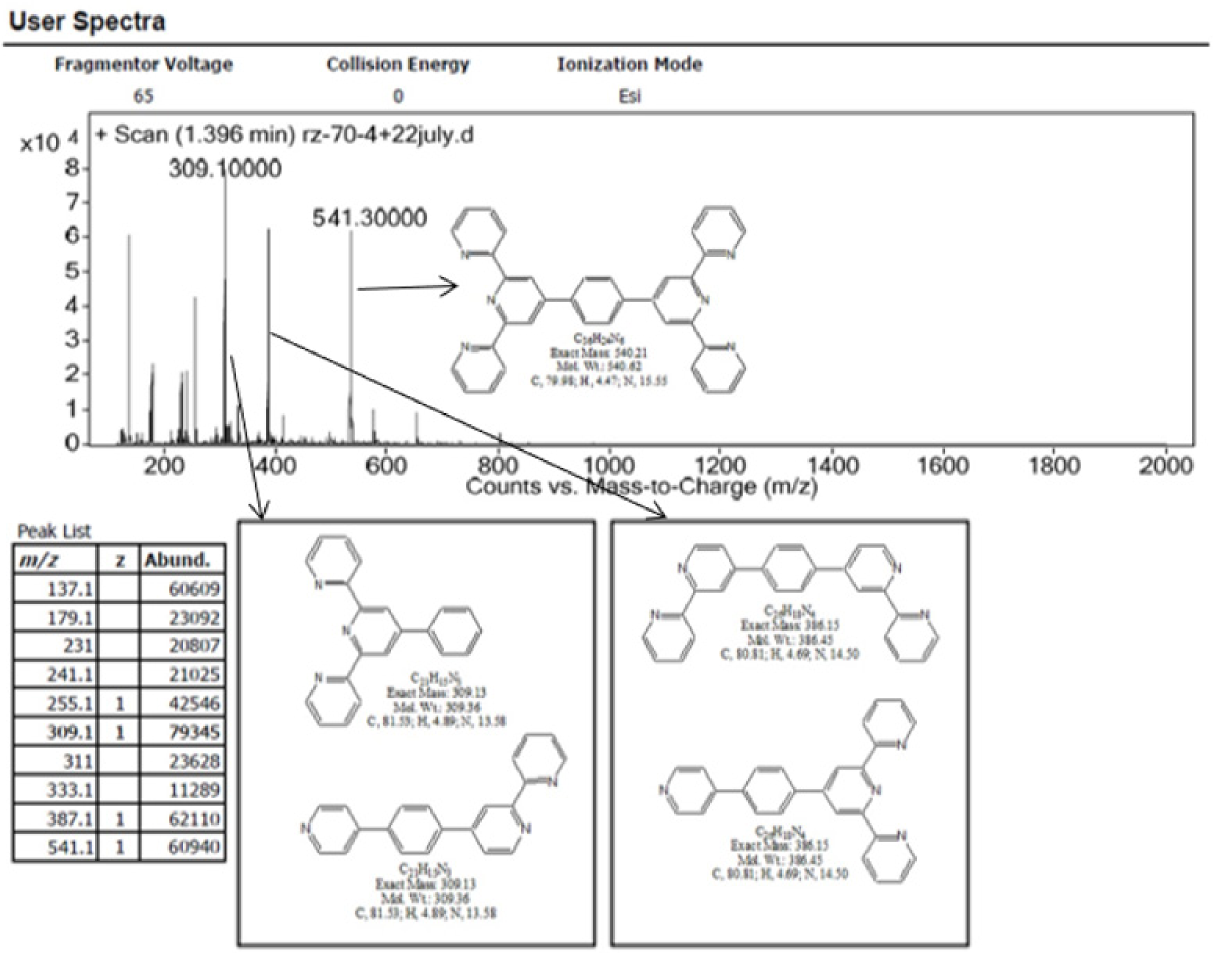


Figure 3: The FTIR (KBr) spectrum of (I).



Peak List

m/z	z	Abund.
137.1		60609
179.1		23092
231		20807
241.1		21025
255.1	1	42546
309.1	1	79345
311		23628
333.1		11289
387.1	1	62110
541.1	1	60940

Figure 4: The LC-MS spectrum of (I): m/z 541.3 ([M+H] +), 387.1 ([(M-2py+H)] +), and 309.1 ([(M-3py+H)] +).

The ^{1}H NMR spectrum corresponding to the ligand (I) (Figure 2) was consistent to the data reported earlier. The singlet peak at σ 8.86 is a characteristic signal associated to the four equivalent of single H3′ in pyridine rings in the middle of terpyridyl domains (2-pyridyl) and the singlet peak at σ 8.08 assigned to the four equivalent protons of the benzene ring in the middle. The FTIR spectrum of ligand (I) (Figure 3) shows peaks at 1687 cm^{-1} and 1568 cm^{-1} assigned for aromatic C=N double bond stretching frequency in pyridine rings. The broad peak at 3439 cm^{-1} also assigned for the presence of EtOH which is consistent with the elemental analysis of the compound. LC-MS spectrum of the ligand (I) (Figure 4) also shows three significant peaks at *m/z* 541.3 ([M+H]$^+$), 387.1 ([(M-2py+H)]$^+$), and 309.1 ([(M-3py+H)]$^+$).

Experimental

Reagent grade commercial compounds were used as starting materials, and their purity was checked by ^{1}H and ^{13}C NMR. The 400 MHz 1H NMR spectra were acquired on a Bruker-400 spectrometer. ^{1}H NMR chemical shifts are reported relative to tetramethylsilane. Infrared spectra (400-4000 cm^{-1}) were obtained using a Shimadzu 8201PC Series FTIR interfaced with an Intel 486 PC operating Shimadzu HyperIR software. Spectra were obtained using diffuse reflectance method in solid KBr. GC-MS, LC-MS and Microanalyses were performed at Shahid Beheshti University of Medical Sciences. Melting points of organic compounds were determined using Electrothermal IA 9200 with microprocessor heating oven control melting point apparatus without corrections.

Synthesis of 1,4-bis(2,2′:6′,2′′-terpyridin-4′-yl)benzene (I): To a 500 mL double-necked round bottom flask containing benzene-1,4-dicarbaldehyde (2.68 g, 20 mmol) in 200 mL EtOH was added 2-ccetylpyridine (10.0 mL, 90 mmol) dropwide with stirring at r.t. The reaction mixture was allowed to stir for about 8 hrs. during which a white precipitate was formed in orange solution. The small amount of the precipitate was taken for characterisation. The white compound which was taken from bulk mixture was washed thoroughly with EtOH and dried for FTIR and elemental analyses. The compound was characterised as tetraketone 1,4-bis[1,5-dioxo-1,5-bis(2-pyridyZ) pentan-3-yl]benzen (3). Anal. Calc. for

$C_{36}H_{30}N_4O_4$ (582.23): C 74.21, H 5.19, N 9.62%; found: C 74.09, H 5.32, N 9.74%. IR spectrum, υ, cm-1: 3433.89 (O-H), 1700.69. To the reaction mixture was added ammonium acetate (5.0 g) over a period of 10 min. The reaction mixture was connected to reflux and allowed to stir at refluxing temperature for 72 hrs. The mixture was cooled to r.t and the precipitate was collected by filtration then washed with EtOH and dried to obtain the desired ligand as an off-white solid (84%, 9.07 g, 16.79 mmol). Mp > 200 ^{o}C. 1H NMR ($CDCl_3$) δ 8.86 (s, H3′), 8.79 (d), 8.73 (d), 8.11 (s, benzene ring), 7.94 (dd), 7.41 (dd). MS: *m/z* 541.3 ([M+H]$^+$), 387.1 ([(M-2py+H)]$^+$), 309.1 ([(M-3py+H)]$^+$). Anal. Calc. for $C_{36}H_{24}N_6{\bullet}C_2H_5OH$ (586.25): C 77.79, H 5.15, N 14.32%; found: C 77.61, H 5.29, N 14.51%. IR spectrum, υ, cm^{-1}: 3439 (presence of molecular EtOH), 1687 cm^{-1} and 1568 cm^{-1} (C=N).

Acknowledgments

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Conflict of Interest

The authors declare that they have no conflict of interest.

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