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NOTE

Synthesis of the New Thiophene Ligand and its Macroacyclic Complexes with Ni^{2+} and Cu^{2+}

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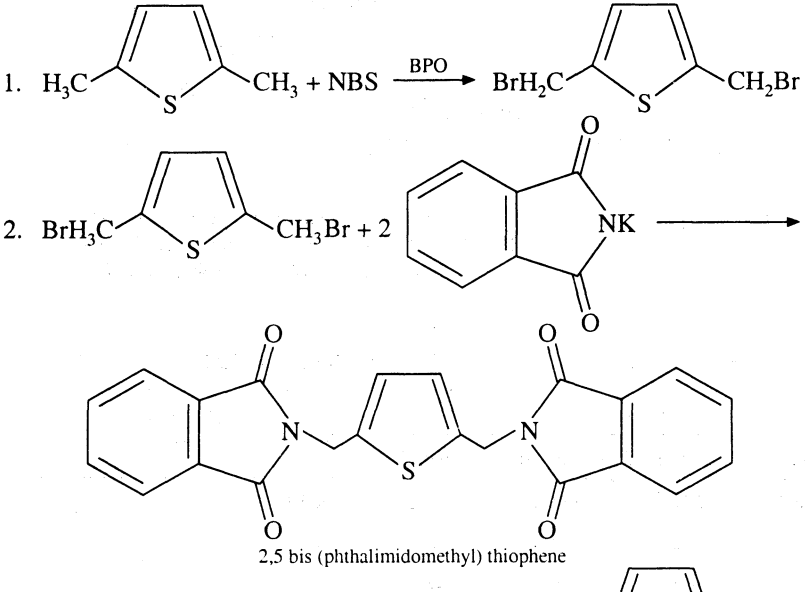
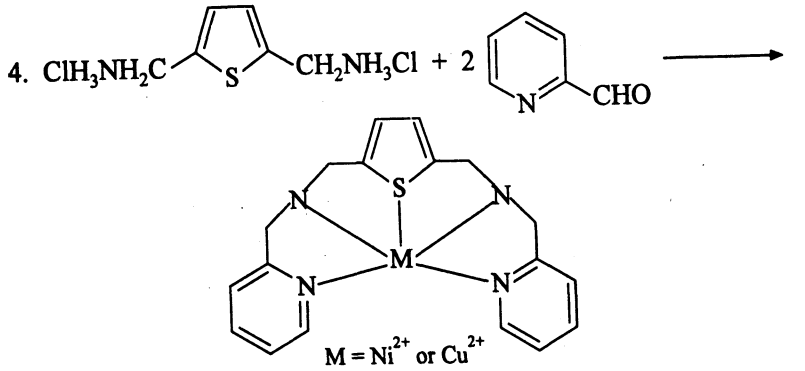
The new macroacyclic Schiff base ligand was prepared by the condensation of 2,5-bis(aminomethyl)thiophene with 2-formylpyridine, and the relevant Ni^{2+} and Cu^{2+} complexes synthesized simultaneously as well. IR, NMR and CHN techniques were used for structural characterization.

Key Words: Schiff base ligand, Thiophene, Complex.

Schiff base played a central role as chelating ligands in main group and transition metal coordination chemistry[1]. Although a large number of complexes of structural types of $M(N_3O_2)$, $M(N_2O_2S)$, $M(N_3S_2)$, and $M(N_4O)$ have been synthesized and characterized, complexes of the pentadentate N_4S Schiff base ligands are rather scarce[1, 2]. Therefore, we synthesized such Schiff base ligands, formed by condensation of 2-pyridyl aldehydes with amine ligands as below:





According to the spectral information, two IR bands at 1657 and 1643 cm^{-1} in both complexes are related to the imine ν(C=N) bands. Also, four IR bands at 1597, 1570, 1599 and 1576 cm^{-1} are related to the pyridine ν(C=N) and ν(C=C) bands. According to the analytical calculations, the nickel complex has only one nickel nucleus, while in the copper complex, two copper nuclei can be seen. All spectral informations are as following:

2,5-Bis(bromomethyl)thiophene

IR (KBr), ν (cm^{-1}): 3000, 1625, 1460, 800, 610 cm^{-1}; ^1H NMR (CCl_4, 60 MHz); δ = 4.75 (s, 4H), 7.02 (s, 2H).

2,5-Bis(phthalimidomethyl)thiophene

IR (KBr), ν (cm^{-1}): 1765, 1710, 1459; ^1H NMR (d_6-acetone, 90 MHz); δ = 4.86 (s, 4H), 6.91 (s, 2H), 7.84 (s, 8H).

2,5-Bis(aminomethyl)thiophenedihydrochloride

IR (KBr), ν (cm^{-1}): 3000–2700, 1591, 1480; ^1H NMR (DMSO-d_6, 90 MHz); δ = 4.17 (s, 4H), 7.19 (s, 2H), 8.72 (s, 6H). ^{13}C NMR (DMSO-d_6, 90 MHz); δ = 36.67, 128.1, 135.45.

Ni(II) Complex

IR (paraffin), ν (cm^{-1}): 2800, 1657, 1597, 1570, 1100. Anal. (%): Calcd. for $C_{18}H_{16}N_4NiS(ClO_4)_2$: C: 37.39, H: 3.46, N: 9.69; Found C: 37.40, H: 4.00, N: 9.51.

Cu(II) Complex

IR (paraffin), ν (cm^{-1}): 2800, 1643, 1599, 1576. Anal. (%): Calcd. for $C_{18}H_{16}Cu_2N_4SCl_2{\cdot}3H_2O$: C: 37.72, H: 3.49, N: 9.78; Found C: 37.87, H: 3.82, N: 10.25.

Infrared spectra were recorded on Shimadzu IR-435 spectrometer. ^1H NMR and ^{13}CNMR spectra were recorded on Jeol FX-FT 90Q spectrometer. CHN were measured on a CHN-O-Rapid, Foss-Heraeus. Melting points were determined on a Stuart Scientific apparatus.

Preparation of 2,5-bis(bromomethyl)thiophene: To a stirred solution of 2,5-dimethylthiophene (2.3 mL, 20 mmol) and dibenzoyl peroxide (0.07 g, 0.29 mmol) in CCl_4 (15 mL), was slowly added N-bromosuccinimide (7.12 g, 40 mmol) and dibenzoyl peroxide (0.07 g, 0.29 mmol). The reaction mixture was

heated under reflux for 4 h. After cooling to room temperature, the solution was filtered and CCl_4 removed under reduced pressure. The residue obtained was recrystallized by petroleum ether (40–60). Brown crystal has m.p. *ca.* 66–68°C (yield: 4.04 g, 74%)[3–5].

Preparation of 2,5-bis(phthalimidomethyl)thiophene: A solution of 2,5-bis(bromomethyl)thiophene (4 g, 14.8 mmol) in DMF (20 mL) was added dropwise to a solution of potassium phthalimide (5.48 g, 29 mmol) in DMF (30 mL). The reaction mixture was stirred for 1 h at 120°C. Water (400 mL) was then added to the cooled reaction mixture and the brown precipitate was filtered and washed with diethyl ether (2 × 10 mL) and dried *in vacuo.* Melting point of the brown crystal was about 257–259°C (yield: 5 g, 85%).

Preparation of 2,5-bis(aminomethyl)thiophenedihydrochloride: 2,5-bis-(phthalimidomethyl)thiophene (5 g, 12.4 mmol) was dissolved in a mixture of glacial HOAc (100 mL) and 35% w/w HCl (100 mL) and heated to reflux for 72 h. After cooling to room temperature, the solution was filtered, the filtrate concentrated *in vacuo,* and water (10 mL) was added. The solution was filtered again, and the filtrate concentrated *in vacuo.* Dry ethanol (30 mL) was then added, and the solution was put in a fridge, and the brown crystals obtained (yield: 1.6 g, 60%).

Preparation of complexes

Ni(II) Complex: Solid NaOH (0.037 g, 0.93 mmol) was added to the solution of 2,5-bis(aminomethyl)-thiophene (0.1 g, 0.46 mmol) in dry ethanol (20 mL) and stirred for 0.5 h. The solution was filtered and the filtrate was added to the solution of nickel(II) nitrate (0.13 g, 0.45 mmol) and 2-formylpyridine (0.1 g, 0.93 mmol) in dry ethanol (20 mL) and stirred for a further 1 h at 60°C. After cooling to room temperature, the reaction mixture was filtered and sodium perchlorate (0.055 g, 0.45 mmol) was added to the filtrate. The obtained precipitate was washed with methanol and dried *in vacuo* (yield: 0.11 g, 64%).

Cu(II) Complex: Solid NaOH (0.037 g, 0.93 mmol) was added to the solution of 2,5-bis(aminomethyl)-thiophene (0.1 g, 0.46 mmol) in dry ethanol (20 mL) and stirred for 0.5 h. The solution was filtered and the filtrate was added to the solution of copper(II) choloride (0.08 g, 0.46 mmol) and 2-formylpyridine (0.1 g, 0.93 mmol) in dry ethanol (20 mL), and stirred for a further 1 h at 60°C. After cooling to room temperature, the obtained precipitate was washed with methanol and dried *in vacuo* (yield: 0.11 g, 64%).

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