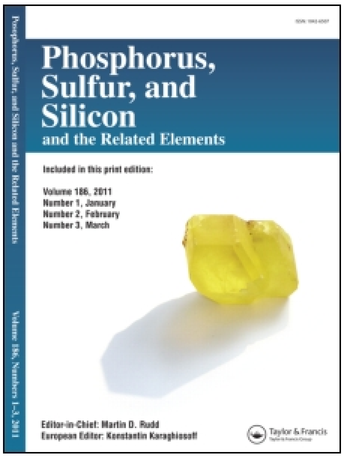

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SYNTHESIS OF THE NEW SCHIFF BASE POLYAZA MACROCYCLES AND THEIR COMPLEXES WITH Cu^{2+} AND Ni^{2+}

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SYNTHESIS OF THE NEW SCHIFF BASE POLYAZA MACROCYCLES AND THEIR COMPLEXES WITH Cu^{2+} AND Ni^{2+}

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The new Schiff base macrocycles were synthesized from the condensation of diethylenetriamine or dipropylenetriamine with terephthalaldehyde. The relevant transition metal complexes were then formed with nickel and copper salts after the reduction of the macrocycles. CHN-analysis, IR, NMR, and mass spectroscopies were used for their structure characterization.

Keywords: Complexes; ligand; macrocycles

In recent years, polyaza macrocyclic ligands with rigid structure units have played important roles in transition metal complexes.[1–3] This importance is due to both the kinetic and thermodynamic stabilities of their complexes. The study of such ligands as structural models in cellular metabolism is easily possible.[4–6] Many of the natural macrocycles such as porphyrin have an important role for oxygen transfer in hem structure.[7]

Therefore, terephthalaldehyde was used as a rigid dialdehyde in our research project. Condensation of terephthalaldehyde with diethylenetriamine produced two coordination sites for metals which enables the investigation of this system as a mimic model comparing it to the natural oxygen transfer system. Such a Schiff base macrocycle was synthesized in dilute condition in order to inhibit the relevant polymer formation (Scheme 1). The dilute media is not necessary in condensation of terephthalaldehyde with dipropylenetriamine, since the new conformation of the obtained macrocycle resulted from the intramolecular attack of the free amine to the imine bond, which inhibits the polymer formation even in the concentrated condition (Scheme 2).

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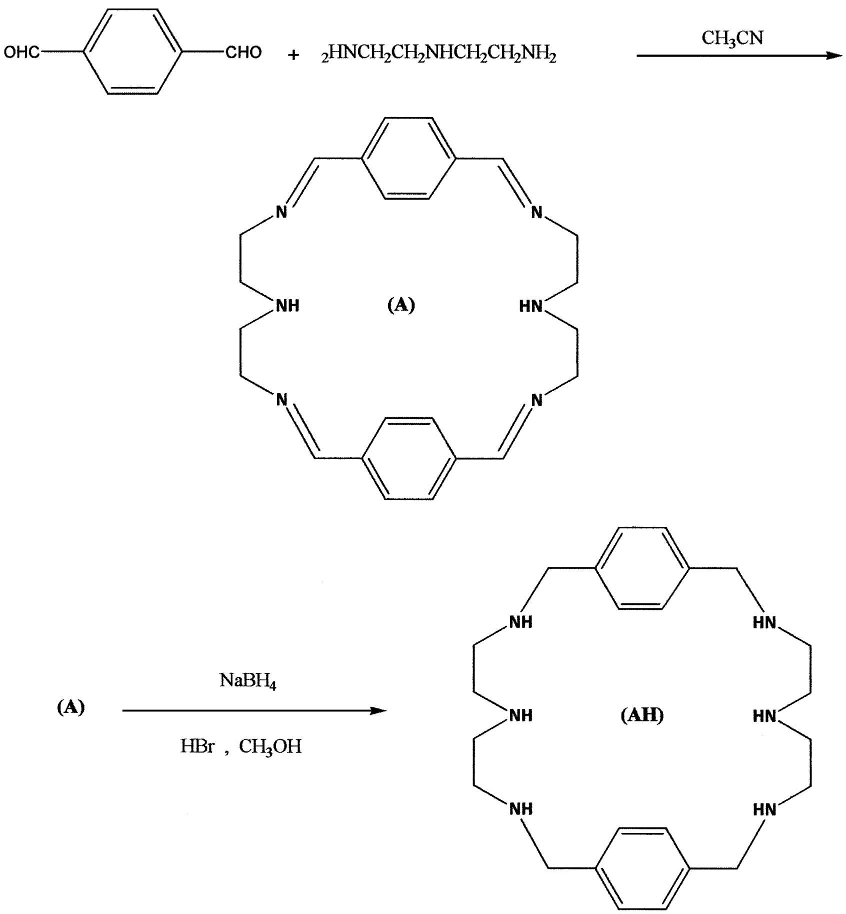
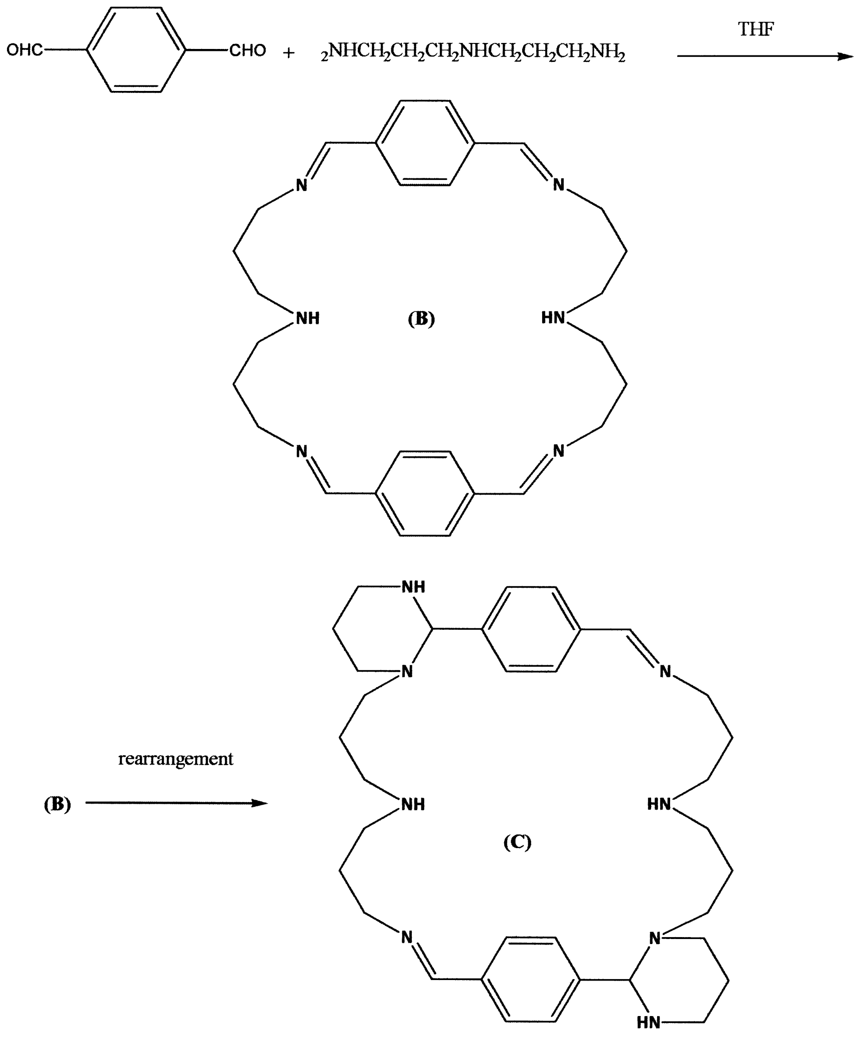


SCHEME 1

IR spectra were recorded on Shimadzu IR-435-U-04 spectrometer. 1HNMR spectra were recorded on FT Bruker BRX-500 MHz, Avence spectrometer, CHN were measured on a CHN-O-Rapid Foss-Heraeus, and Mass spectra obtained on Shimadzu GC-14A. All spectral information are as below:

The Macrocyclic Schiff Base (A): IR (KBr disk): 3300 (N—H), 2900 (C—H), 1645 (C =N), 800 cm^{-1} (*p*-substituted benzene ring). ^{1}HNMR (CDCl$_3$, 500 MHz): 8.298 (s, 4H, CH=N), 7.542 (s, 8H, aromatics), 3.78–3.80 (t, 8H, CH2—N =), 2.987–3.0 (t, 8H, CH2—NH—), 2.1 (m, 2H,—NH—). Anal. Calcd. for $C_{24}H_{30}N_6$: C, 71.61; H, 7.51; N, 20.88, Found: C, 71.64; H, 7.43; N, 20.81. The peak 402 from the mass spectroscopy, indicates the [2 + 2] addition.



SCHEME 2 Despite all attempts, the macrocyclic Schiff base (c) was not reduced, and so the relevant complexes with different metal ions did not form.

The Reduced Macrocycle (AH): IR (KBr disk): 3300 (N—H), 2900 cm^{-1} (C—H). The absence of the 1645 cm^{-1} band due to C=N, confirms the complete reduction to the saturated hexamine macrocycle. ^{1}HNMR (D_2O, 500 MHz): 7.42 (s, 8H, aromatics), 4.225 (s, 8H, benzylic protons), 3.297–3.325 (t, 8H, CH2—NH), 3.146–3.174 (t, 8H, CH2—NH). Anal. Calcd. for $C_{24}H_{38}N_6.6HBr.6H_2O$: C, 28.68; H, 5.57; N, 8.36, Found: C, 28.09; H, 5.08; N, 8.21.

The Macrocyclic Schiff Base (C): IR (KBr disk): 3300(N—H), 2950 (C—H), 1650 (C=N), 1450 (C—C), 900 cm^{-1} (*p*-substituted benzene ring). ^{1}HNMR ($CDCl_3$, 500 MHz): 7.811–7.836 (s, 2H, CH=N), 7.233–7.281 (m, 8H, aromatics), 1.551–3.955 (m, 28H). Anal. Calcd. for $C_{28}H_{38}N_6$: C, 73.0; H, 8.3; N, 18.6, Found: C, 73.2; H, 8.27; N, 18.23. The peak 485 from the mass spectroscopy, indicates the [2 + 2] addition. The ^{1}HNMR data show that in condensation of dipropylenetriamine to terephthaladehyde, the intramolecular attack of the free amine to the imine bonds inhibits the formation of the macrocyclic Schiff base (B).

Ni(II) complex of (AH): IR (paraffin): 3270 (N—H), 1504 (acetate groups, unsymmetric), 1450 (acetate group, symmetric), 1100 cm^{-1} (perchlorate ions, Cl—O). Anal. Calcd. for $C_{28}H_{44}N_6O_{12}Cl_2Ni_2.2H_2O$: C, 10.43; H, 6.18; N, 37.58, Found: C, 9.54; H, 5.45; N, 38.16 (Scheme 3).

Cu(II) complex of (AH): IR (paraffin): 3600 (O—H), 3250 (N—H), 1100 cm^{-1} (perchlorate ions, Cl—O). Anal. Calcd. for $C_{24}H_{38}N_6O_{16}Cl_4Cu_2\cdot 4H_2O$: C, 28.59; H, 4.56; N, 8.34, Found: C, 29.59; H, 5.00; N, 8.94.

Preparation of the Macrocyclic Schiff Base (A)

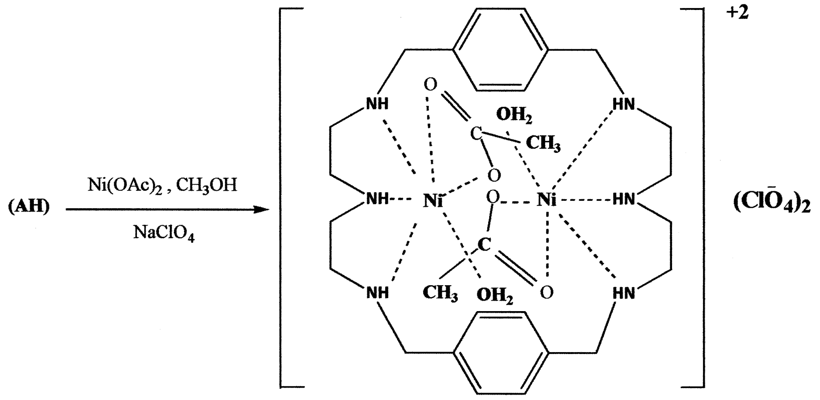
To a stirred solution of diethylenetriamine (0.972 ml, 9 mmol) in dry acetonitrile (280 mL), was added dropwise a solution of terephthalaldehyde (1.2 g, 9 mmol) in dry acetonitrile (150 mL) in room temperature. After 2 days, the yellowish white precipitate was separated, washed with diethyl ether (2 × 20 mL) and dried in vacuum. The precipitate was then recrystallized in toluene. Yield 1.34 g, 75%. The crystal has melting point ca 155–157°C.

Preparation of the Reduced Macrocycle (AH)

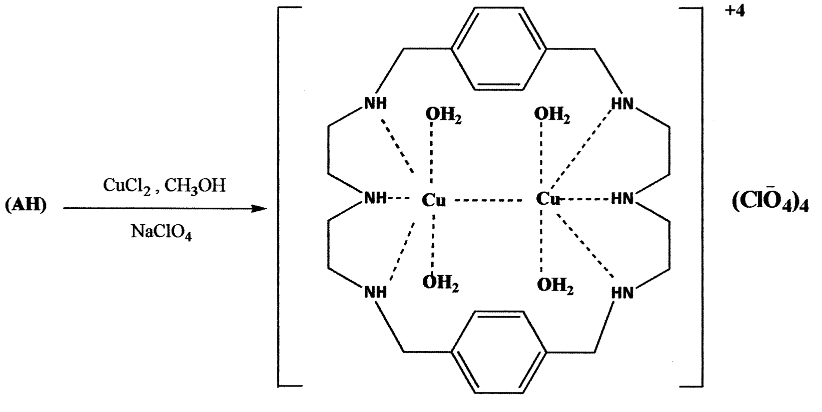
The macrocyclic Schiff base A (1.5 g, 3.7 mmol) was dissolved in methanol (10 mL) and heated up to 40°C. NaBH4 (0.9 g, 23 mmol) was added slowly during 2–3 h with stirring, and heated for further 3 h. Methanol was removed by rotary evaporator and chloroform (20 mL) was added. The obtained suspension was filtered and chloroform removed from the filtrate. The solution of 48% HBr (10 mL) and ethanol (50 mL) was added to the precipitate, filtered, and dried in vacuum at room temperature. Yield 1.5 g, 45%.

Preparation of the Macrocyclic Schiff Base (C)

To a stirred solution of dipropylenetriamine (1.26 mL, 9 mmol) in dry THF (50 mL), was added dropwise a solution of terephthalaldehyde (1.2 g, 9 mmol) in dry THF (50 mL) at −5°C. After 24 h, the white



binuclear Ni complex, $C_{28}H_{44}N_6O_{12}Cl_2Ni_2 \cdot 2H_2O$



binuclear Cu complex, $C_{24}H_{46}N_6O_{20}Cl_4Cu_2$

SCHEME 3

precipitate was separated, washed with diethyl ether (2 × 20 mL), and dried in vacuum. The precipitate was then recrystallized in toluene. Yield 1.4 g, 70%. The crystal has melting point ca. 167°C.

Preparation of Ni(II) Complex of (AH)

The reduced macrocycle AH (0.45g, 0.5 mmol) was dissolved in ethanolic NaOH (0.14 g, 3 mmol) and ethanol removed by heating. The precipitate extracted with dichloromethane and the solvent removed by rotary evaporator. The oily product dissolved in methanol (10 mL), and the solution of nickel acetate (0.17 g, 1 mmol) in methanol (10 mL) was then added. After addition of sodium perchlorate (0.135 g, 1 mmol), the mixture was kept at room temperature for further 3 h. The blue precipitate filtered and recrystallized in methanol. Yield 25 g, 60%.

Preparation of Cu(II) Complex of (AH)

The reduced macrocycle AH (0.45 g, 0.5 mmol) was dissolved in ethanolic NaOH (0.14 g, 3 mmol) and ethanol removed by heating. The precipitate extracted with dichloromethane and the solvent removed by rotary evaporator. The oily product dissolved in methanol (10 mL), and the solution of copper chloride (0.134 g, 1 mmol) in methanol (10 mL) was then added. After addition of sodium perchlorate (0.27 g, 2 mmol), the mixture was kept at room temperature for further 3 h. The bluish green precipitate filtered and recrystallized in methanol. Yield .25 g, 60%.

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