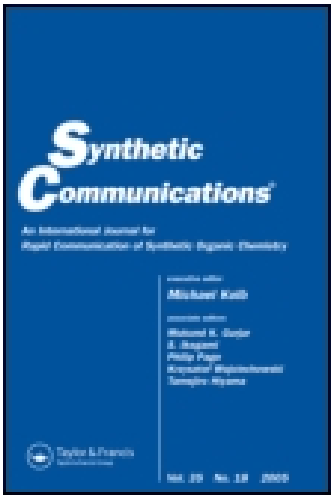

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Synthesis and Characterization of Some New Star-Shaped Polydentate Ligands from 2,4,6-Trichloro-1,3,5-triazine

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW STAR-SHAPED POLYDENTATE LIGANDS FROM 2,4,6-TRICHLORO-1,3,5-TRIAZINE

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Some new star-shaped polydentate ligands were synthesized using 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine as a template and were characterized by infrared, ^{1}H NMR, and ^{13}C NMR spectra and elemental analysis. These products may form polynuclear complexes with metal ions, and the complexes may possess potential applications in the area of electromaterials, optomaterials, magnetic materials, and bio-organic materials.

Keywords: Schiff base; star-shaped polydentate ligands; 1,3,5-triazine derivatives; triazole derivatives

INTRODUCTION

1,3,5-Triazine derivatives have been known for a long time. They have found widespread applications in the pharmaceutical, textile, plastic, and rubber industries and are used as pesticides, dyestuffs, optical bleaches, explosives, and surface active agents.[1] These s-triazine derivatives are mostly synthesized from cyanuric chloride because of the stability of triazine ring and the controllability of the nucleophilic substitution reaction of its chlorine atoms. The reactivity of the three chlorine atoms of cyanuric chloride is very high, which makes its substitution reaction very easy, but the reactivity degree of the chlorine atoms is different: by controlling the temperature, 2,4,6-mono, di-, or tri-substituted triazine derivatives can be obtained in a one-pot synthesis by sequential selective addition of nucleophiles. Furthermore, cyanuric chloride is a very inexpensive reagent and easily available, which are some of the reasons that s-triazine derivatives are widely applied.

In recent years, there has been a growing interest in the design and synthesis of supramolecular polynuclear mental complexes[2,3] because of their potential applications in magnetism, catalysis, electrical conductivity, and nonlinear optics.[4–8] The preparation of polymetallic complexes can be achieved by using rationally designed polydentate ligands.[9] 1,3,5-Triazine derivatives, where the heteroaromatic ring is implicated in crucial supramolecular interactions, that is, hydrogen bonds and/or

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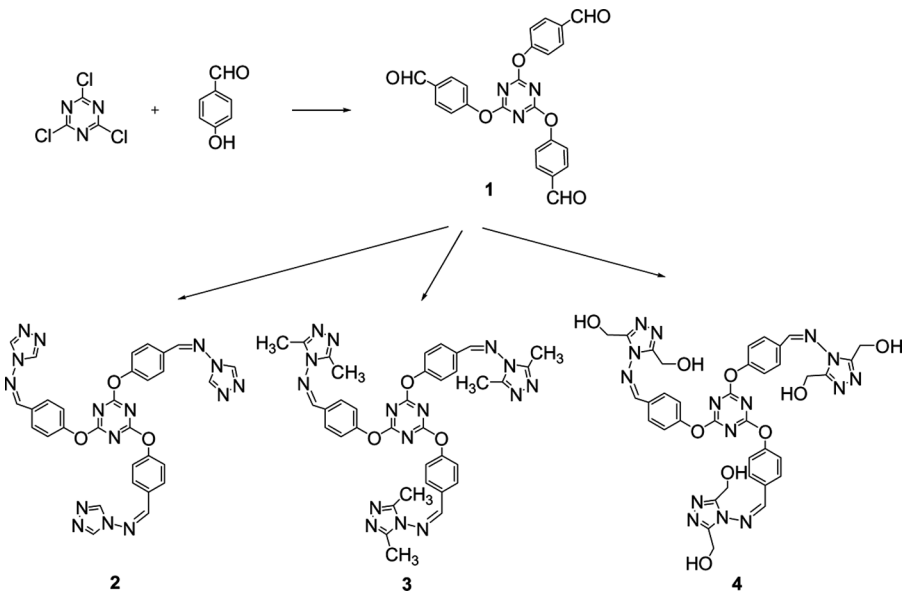
π interactions,[10] have found tremendous applications in the field of supramolecular chemistry.[11] Some rigid and flexible polydentate 1,3,5-triazine-based ligands were designed and synthesized as building blocks for (supramolecular) polymers. It is worth mentioning that the use of a flexible building block with inherent conformational freedom may imply the existence of various supramolecular isomers.[12]

Our present aim was to prepare some new star-shaped polydentate ligands using 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (**1**) as the template. These compounds may have the ability to form polynuclear complexes with different metal ions, and the complexes may have potential applications in electromaterials, optomaterials, magnetic materials, bio-organic materials, and so on.

RESULTS AND DISCUSSION

Some new star-shaped polydentate ligands **2**, **3**, and **4** were obtained using the synthetic methods outlined in Scheme 1. 2,4,6-Tris(p-formylphenoxy)-1,3,5-triazine (**1**) was prepared by the reaction of 3 equiv. excess of p-hydroxybenzaldehyde and 1 equiv. of 2,4,6-trichloro-1,3,5-triazine in dioxane at 90 °C for 12 h: triethylamine was used to trap the HCl formed during the substitution reaction. Compound **1** was isolated and recrystallized from ethyl acetate, and the yield reached 89%, higher than with the published methods.

Compound **2** was synthesized by the reductive amination of 1 equiv. of **1** and 3 equiv. excess of 4-amino-1,2,4-triazole under refluxed condition in glacial acetic acid. Infrared (IR) indicated the disappearance of aldehyde. However compounds **3** and **4** were not gained when we used the same synthetic method as used for compound **2**.



Scheme 1. Synthesis of the polydentate ligands.

During the experiment, we found that controlling the reaction temperature was important. When the temperature was decreased, compounds **3** and **4** were obtained in good yields. After repeating the experiment, the best reaction conditions were identified.

CONCLUSION

A simple method to synthesize some new star-shaped polydentate ligands has been developed. These ligands were easily obtained in good yield starting from low-cost, commercially available materials. The products were characterized by Fourier transform (FT)–IR, ^{1}H NMR, and ^{13}C NMR spectra and elemental analysis. The synthesis of complexes from these ligands and different metal ions is currently in progress.

EXPERIMENTAL

Material and Physical Measurement

All reagents were obtained from commercial suppliers and used without further purification. Solvents used for the reactions were purified and dried by conventional methods. 4-Amino-1,2,4-triazole and its derivatives were synthesized according to the published procedures.[13–15]

Melting points were taken on a SGW X-4 melting-point apparatus. ^{1}H NMR and ^{13}C NMR spectra were obtained at 400 MHz using a Bruker Avance 400 NMR instrument with tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. The IR spectra were determined on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets. Elemental analysis was performed on a Elementar Vario EL III element analyzer.

Syntheses

Synthesis of compound 1. 2,4,6-Trichloro-1,3,5-triazine (1.84 g, 0.01 mol) was dissolved in dioxane (20 ml), and a solution of p-hydroxybenzaldehyde (4.88 g, 0.04 mol) and triethylamine (5.05 g, 0.05 mol) in dioxane (40 ml) was added dropwise at room temperature. The mixture was stirred at 90 °C for 12 h. The reaction mixture was then cooled, and the solid was removed by filtration. The filtrate was concentrated, and a white powder was obtained. The white powder was washed with 10% Na_2CO_3 and dried in vacuo. Then the powder was recrystallized from 40 ml of ethyl acetate to afford 3.92 g of a white fluffy precipitate: yield = 89%, mp 174–176 °C. IR (KBr) ν 2833, 1701, 1568, 1361, 1211, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.26 (d, 6H, $J = 8.4$ Hz), 7.86 (d, 6H, J = 8.4 Hz), 9.95 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ 122.2, 131.0, 134.0, 155.0, 172.6, 191.8 ppm. Elemental analyses found (calcd.): C, 65.35 (65.31); H, 3.42 (3.43); N, 9.50 (9.51).

Synthesis of compound 2. 4-Amino-1,2,4-triazole (0.25 g, 3×10^{-3} mol) was added to a solution of 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (0.22 g, 0.5×10^{-3} mol) in 10 ml of glacial acetic acid. The reaction mixture was heated under reflux for 4 h. The solvent was then removed in vacuo, and the remaining residue was

washed with methanol and chloroform. After being dried in vacuo, a white solid was obtained: yield 76%. IR (KBr) ν 3103, 1560, 1498, 1365, 1211, 842 cm^{-1}. ^1H NMR (DMSO) δ 7.47 (d, 6H, $J = 8.4$ Hz), 7.92 (d, 6H, $J = 8.4$ Hz), 9.09 (s, 3H), 9.12 (s, 6H) ppm. ^{13}C NMR (DMSO) δ 122.3, 129.7, 130.0, 138.8, 153.9, 157.0, 172.7 ppm. Elemental analyses, found (calcd.): C, 56.39 (56.34); H, 3.32 (3.31); N, 32.88 (32.85).

Synthesis of compound 3. The synthesis was identical to compound 2, using 4-amino-3,5-dimethyl-1,2,4-triazole instead of 4-amino-1,2,4-triazole. The mixture was heated at 70 °C for 15 h, and the product was washed with methanol: yield 88%. IR (KBr) ν 3358, 1566, 1504, 1363, 1209, 848 cm^{-1}. ^1H NMR (DMSO) δ 2.24 (s, 18H), 7.36 (d, 6H, $J = 8.4$ Hz), 7.90 (d, 6H, $J = 8.4$ Hz), 8.72 (s, 3H) ppm. ^{13}C NMR (DMSO) δ 10.6, 122.2, 130.1, 130.9, 147.2, 154.3, 162.9, 172.8 ppm. Elemental analyses, found (calcd.): C, 59.77 (59.74); H, 4.59 (4.60); N, 29.08 (29.05).

Synthesis of compound 4. A mixture of 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (0.22 g, 0.5×10^{-3} mol) and 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole (0.43 g, 3×10^{-3} mol) in 10 ml of glacial acetic acid was heated at 70 °C for 15 h, and a white precipitate was formed. Then the mixture was filtered, and the product was washed with methanol. After being dried in vacuo, a white solid was obtained: yield 84%. IR (KBr) ν 3257, 3223, 1570, 1367, 1205 cm^{-1}. ^1H NMR (DMSO) δ 4.51 (d, 12H), 5.51 (t, 6H), 7.37 (d, 6H, $J = 8.8$ Hz), 7.87 (d, 6H, $J = 8.8$ Hz), 8.88 (s, 3H) ppm. ^{13}C NMR (DMSO) δ 53.2, 122.1, 130.2, 130.3, 151.0, 154.2, 162.6, 172.8 ppm. Elemental analyses, found (calcd.): C, 52.80 (52.75); H, 4.07 (4.06); N, 25.61 (25.63).

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