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SYNTHESISAND CHARACTERIZATION OF A NEW THIAAZACROWN ETHERDERIVED FROM NAPHTHALIMIDE

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ABSTRACT

A new thiaazacrown ether derived from naphthalimide was successfully synthesized with high dilution method in high yields. The structure of this new compound was characterized by NMR and MS.

INTRODUCTION

Crown ethers show strong ability to form remarkably stable and selective complexes with heavy metal ions and have been found to exhibit interesting host-guest complexation characteristics (Zhang *et al.*, 2010; Yu *et al.*, 2013). Among them, crown ethers containing nitrogen and sulfur donor atoms (i.e. thiaazacrown ethers) are of special interest as they exhibit extremely high affinities towards heavy metal ions (Sang *et al.*, 2012; Nikac *et al.*, 2010; Zhang *et al.*, 2011), so the design and synthesis of mixed-donor crown ethers has been developed rapidly because of its applications in the field of coordination chemistry. Several synthetic methods for the construction of crown ethers have been developed (Krakowiak *et al.*, 1989), among them the high dilution method is most popular (Elwahy and Abbas, 2000). The reactions proceed to give '1+1' macrocycles or '2+2' macrocycles depending on the chain length of starting materials (Elwahy and Abbas, 2000). In this experiment, a new thiaazacrown ether derived from naphthalimide was successfully synthesized with the high dilution method in high yields (Scheme). The structure of this new compound was characterized by NMR and MS.

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Experimental Section

Reagents and Instruments

All reagents and solvents are of analytical grade and used without further purification. Nuclear magnetic resonance (NMR) spectra were measured with a Brucker WM-500 instrument and chemical shift were given in ppm from tetramethylsilane (TMS). Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100.

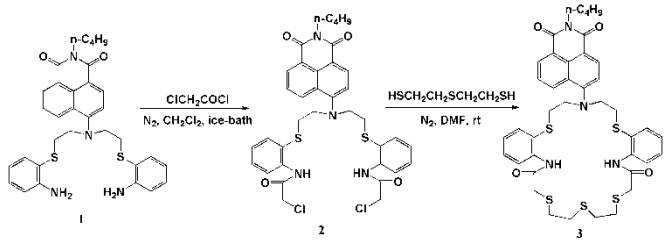
Synthesis of thiaazacrown ethers

Compound 1 and 2 was synthesized as described before (Zhang *et al.*, 2012). Synthesis of thiaazacrown ether 3: Monoazathiacrown ethers 3 were synthesized as described before (Zhang *et al.*, 2010). A solution of 2 (0.5 mmol) in DMF (50 mL) and that of 2, 2'-thiodiethanethiol (0.5 mmol) in DMF (50 mL) were added simultaneously to a solution of DMF (50 mL) containing 2 mmol anhydrous Na_2CO_3. The whole process was operated under nitrogen atmosphere with vigorously stir for 15 h. The resulting mixture was poored into cold water and the precipitate so obtained was filtered and dried in vacuum. Yields: 92%. MS m/z: 805.03 $[M+H]^+$. ^1H NMR (δ: ppm, $CDCl_3$): 9.69 (s, 2H, NH), 8.54-8.55 (d, 1H,

ArH), 8.42-8.44 (d, 1H, ArH), 8.29-8.31 (d, 2H, ArH), 8.22-8.23 (d, 2H, ArH), 8.09 (s, 1H, ArH), 7.56-7.59 (t, 1H, ArH), 7.23-7.28 (m, 5H, ArH), 7.14-7.16 (d, 1H, ArH), 6.89-6.91 (t, 2H, ArH), 4.15-4.18 (t, 2H, $-CH_2N$), 3.51-3.54 (t, 4H, NCH_2-), 3.45 (s, 4H, $C=OCH_2$-), 2.92-2.95 (t, 4H, SCH_2-), 2.90-2.91 (t, 4H, SCH_2-), 2.88-2.89 (t, 4H, SCH_2-),1.68-1.73 (m, 2H, $-CH_2CH_2CH_3$), 1.41-1.48 (m, 2H, $-CH_2CH_3$), 0.96-0.99 (m, 3H, $-CH_3$). ^{13}C NMR (δ: ppm, $CDCl_3$): 166.76, 164.29, 163.80, 162.54, 152.17, 138.76, 134.54, 131.54, 131.32, 129.96, 129.84, 129.82, 127.12, 126.13, 124.61, 123.26, 122.49, 120.44, 117.77, 117.49, 53.11, 40.12, 37.76, 36.47, 33.78, 33.36, 32.08, 31.42, 30.22, 20.36, 13.83.

RESULTS AND DISCUSSION

Design and synthesis of mixed-donor crown ethers developed rapidly because of its wide applications in the field of coordination chemistry. Several synthetic methods for the crown ethers have been reported (Krakowiak *et al.*, 1989), among them the template method and high dilution method are most popular. Because it's difficult to elute the template ions, so the application of the template method was limited.



Scheme Synthesis route of thiaazacrown ether

In this work, a novel 24 membered azathiacrown ether 3 was synthesized with high dilution method in high yields. The starting materials of 1 with chloroacetylchloride formed the oil compounds 2 in high yields, and then used directly without further purification. Subsequent cyclization of 2 with 2, 2'-thiodiethanethiol in DMF in the presence of anhydrous Na_2CO_3 under nitrogen atmosphere at room temperature produced the corresponding macrocycle 3 in 92% yields. The structure of the target compound was characterized by MS and NMR spectra. Indeed, the MS spectra data supported the formation of the intermediate and target compounds. The formation of macrocycle is confirmed by the appearance of SCH_2 protons at δ ~2.90 ppm in the ^1H NMR spectrum of compounds 3 in $CDCl_3$.

Conclusions

A novel naphthalimide based thiaazacrown ether was successfully designed and characterized in high yields. The synthesis route was simple and easy to handle.

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