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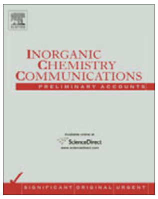

The synthesis and characterization of novel metalloporphyrazine containing crown ether linked calix[4]arene moieties

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ABSTRACT

The synthesis and characterization of novel magnesium porphyrazine, peripherally symmetrically derived from 1,3-alternate 26,28-[35,36-dicyano-34,37-dithia-29,32,40,43-tetraoxa-35-en]calix[4]arene-crown-5, were carried out. This compound was prepared starting from *cis*-1,2-dicyano-1,2-ethylenedithiolate and 1,3-alternate 26,28-bis(5′-chloro-3′-oxapentyloxy)calix[4]arene-crown-5. The new macrocycle was characterized using the techniques of UV–vis, ^{1}H, ^{13}C NMR, IR, MS and elemental analysis.

Porphyrazines as being porphyrin-like systems are of great interest for use in a wide variety of applications including studies on catalysis, photodynamic therapy, molecular electronics, magnetic devices, chemical sensors, liquid crystals and nonlinear optics [1]. The synthesis, characterization and application of tetrapyrrolic macrocycles such as phthalocyanines, porphyrins and their aza-analogues have been investigated in many directions [2]. Despite the structural similarity between phthalocyanines and porphyrazines, the latter have been less studied compared to the phthalocyanines [3]. More recently, the preparation and characterization of porphyrazine, namely the template tetracyclization of the disodium maleonitrile dithiolate (Na_2MNT) [4] precursor, have been subject to enhanced interest. A known disadvantage of porphyrazines is their low solubility in common organic solvents [5]. The solubility of these compounds can be increased by the connection of suitable peripheral sites such as crown ethers. Calix[4]arenes belong to the class of compounds known as metacyclophanes and are synthetic cyclic tetramers composed of four phenolic and four methylene moieties [6]. They have long been of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures. Calix[4]arenes constrained to the 1,3-alternate conformation, and more particularly, the 1,3-calix[4]-bis(crown) and aza-crown systems have received more attention due to possible applications as receptors for cations, anions and neutral molecules [7]. These kinds of compounds were found to be exceptionally selective macrocycles for large alkali metal cations for possible applications such as nuclear-waste remediation [8].

The subject of this study was to synthesize novel ion receptors using porphyrazine containing macrotricyclic 1,3-calix[4]bis(crown) in the 1,3-alternate conformation. Synthesis of 1,3-alternate 26, 28-[35,36-dicyano-34,37-dithia-29,32,40,43-tetraoxa-35-en] calix[4] arene-crown-5 [9] (**3**) was carried out as shown in Scheme 1. 1,3-alternate 26,28-bis(5′-chloro-3′-oxapentylloxy)calix[4]arene-crown-5 (**1**) was made to react with an equivalent amount of a suspension of *cis*-1,2-dicyano-1,2-ethylenedithiolate disodium salt (**2**) in acetonitrile under argon. The reaction mixture was heated at reflux temperature for 48 h to give **3**. The purification of **3** for characterization required column chromatography on silica gel using $CHCl_3$:CH_3OH(7:3) as an eluent and gave 35.5% yield. This compound was fully characterized using spectroscopic data and elemental analysis. In $CDCl_3$, its ^{1}H NMR spectrum displayed relatively well-defined resonance signals in the aromatic and aliphatic units corresponding as expected to the typical signals of the precursor compounds. The ^{13}C NMR spectrum of the same compound **3** clearly indicated the presence of cyano and C=C carbons at $\delta = 112.82$ and 123.26 ppm, respectively. The disappearance of C–Cl and the presence of C≡N stretching vibrations at 2173 cm^{-1} seen in the IR spectrum of this compound also confirmed the formation of **3**. The mass spectrum and the elemental analysis of this compound support the condensation reaction between the starting materials (**1** and **2**). The mass spectrum (Fig. 1) contains peaks at $m/z = 882.3$ which correspond to $[M+H_2O]^+$.

Conversion of calix[4]arene-crown-5-substituted dicyano compound **3** into porphyrazinatomagnesium **4** was achieved, according to Linstead and Whalley [10], by co-cyclization of dinitrile using magnesium as the template in *n*-butanol at reflux for 12 h under

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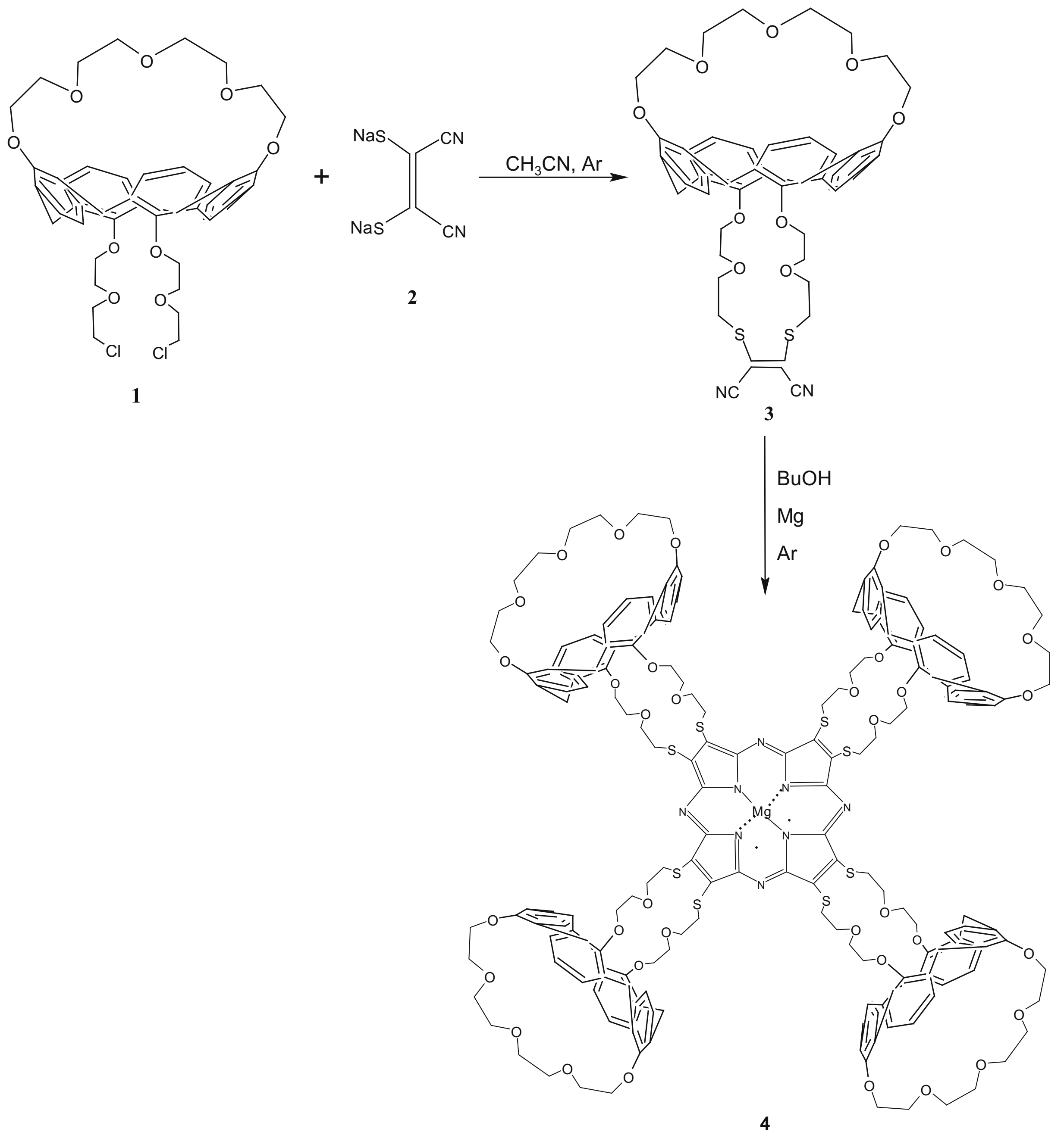

Scheme 1.

argon. The purification of the dark green precipitate was carried out in a soxhlet extractor with chloroform. The solvent was then evaporated to give a deep green–blue metalloporphyrazine as an amorphous solid at a yield of 22%. Since the synthesis of porphyrazines containing macrocyclic units from maleonitrile has been reported [11], the steric hindrance encountered in the present case could be due to appending bulky macrotricyclic groups on **4**. The decrease in yield of the product of this compound could be attributed to this effect [12]. The mass spectrum of this compound (Fig. 2) was measured using the ES/MS technique and the porphyrazinatomagnesium complex displayed a significant peak corresponding to $[M + 2H_2O]^+$ at $m/z = 3491.48$. The elemental analysis data of this compound were also in accordance with the proposed formulation. According to the IR spectrum of **4**, the signals concerning the C≡N groups at 2173 cm^{-1} disappeared and new resonances appeared at 1630 cm^{-1} that are dedicated to the C=N vibrations in the porphyrazine core of **4**. In the ^{1}H and ^{13}C NMR spectra of **4**, the characteristic signals relating to $-CH_2O-$, $-CH_2S-$ and calix[4]arene group in the macrotricyclic groups and porphyrazine skeleton gave significant resonances of the proposed structure. The other carbon-13 NMR signals of **4** [13] are identical to the precursor compound (**3**) except for the C≡N carbons as expected. The chemical shift which appeared at $\delta = 158.56$ ppm of this compound could be related to inner core C=N absorptions [14].

The UV–vis absorption spectra and extinction coefficient of the new magnesium porphyrazinate in chloroform solution (10^{-5} M) at room temperature are shown Fig. 3. The absorption spectrum of magnesium porphyrazinate is typical to that of porphyrazines of D_{4h} symmetry, having a Q-band transition at 668 nm and a shoulder at around 604 nm. The effect of S-substitution on the