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Synthesis and characterization of porphyrazines as novel extractants for the removal of Ag(I) and Hg(II) from aqueous solution

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ABSTRACT

In this study, the synthesis and characterization of new metal-free and metallo-porphyrazines, peripherally and symmetrically derived from 1,3-alternate26,28-[34,37-dithia-29,32,40,43-tetraoxa-35-en]calix[4]arene-25,27-diol, were performed. Dicyano compound was prepared starting from cis-1,2-dicyano-1,2-ethylenedithiolate disodium salt and 1,3-alternate 26,28-bis[2-(2-iodoethoxy)ethoxy]calix[4]arene-25,27-diol, which was prepared by the conversion reaction of 26,28-bis[2-(2-chloroethoxy)ethoxy] calix[4]arene-25,27-diol with NaI. The demetalation of magnesium porphyrazine was achieved by the treatment with trifluoroacetic acid that resulted in the metal-free derivative. The solvent extraction of heavy metal cations such as Ag(I), Hg(II), Cu(II), Mn(II), Cr(III), Ni(II), Pb(II) and Zn(II) by the dicyano compounds and its derived metal-free and magnesium porphyrazines was investigated. From the results of two phase extraction studies on the novel compounds, one can conclude that the metal-free and metallo-porphyrazines show very high selectivity for silver and mercury ions when compared with other metal ions. The novel compounds were characterized using the techniques of UV–vis, ^{1}H, ^{13}C NMR, IR, MS and elemental analysis.

1. Introduction

A large scale of heavy metals was discharged into water environment from mining, Plating plants, metal finishing, dyeing factories and several other industrial processes. Heavy metals in environment are a potential problem to water and soil due to their harmful abilities which can cause hypertension, behavioral changes, learning disabilities inhibition of photosynthesis, oxidative stress and development defects [1–4]. Silver is one of the most important heavy metals but it is non-essential for any living organism. The major source of silver as pollution agent is silver halide which is manufactured for photographic film. Other industrial uses of silver include electronics, jewelry and solder for medical and dental applications [5]. Silver also exhibits strong toxicity to many microorganisms due to some compounds which contain silver and which have been used to prevent the attack of microorganisms [6]. Mercury is one of the most toxic heavy metals and also poses a serious threat to human life and natural environment. It is primarily used in battery, gauges, relay switches, some chemical trades and monometer manufacturings [7]. It has a very high tendency for binding to proteins and due to this relation it mainly affects the renal and nervous systems [8–10].

Calixarenes are a class of macrocyclic compounds in which phenolic groups are linked to many different substituents as 1,3-alternate configuration. The 1,3-calix[4]-crown units have received more attention due to possible applications as receptors for cations, anions and neutral molecules [11–13]. Some calixcrowns possess high selectivity for the alkaline and earth alkaline metal cations among all the synthetic receptors. According to the hard–soft acid–base concept, the better ligands for the "softer" metal cations can be obtained by introducing "softer" sulfur donors into the calixarene skeleton. The calixarene derivatives containing thioether moieties could efficiently extract Ag(I), Hg(II) or Pb(II) [14].

Porphyrazines as being porphyrine-like systems are of great interest for use in a wide variety of applications including studies on catalysis, molecular electronics, magnetic devices, chemical sensors, liquid crystals and non-linear optics [15,16]. Porphyrazines are similar to phthalocyanines so they can also be used in similar applications as phthalocyanines. Porphyrazine derivatives, which contain soft S donor atoms, play an important role in affecting the solid-state interactions. Dithia-crowned porphyrazine offers an advantage over its other analogue counterparts in which two S atoms in each crown unit are in direct conjugation with 18 π-electron core of the porphyrazine [17,18]. The cailx[4]arene

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derivatives containing thioethers could effectively extract some cations such as Pb^{2+}, Hg^{2+} or Ag^{+}. However, the reported calix[4]arenes toward the selectivity for these transition metals was not very satisfying [14,19]. Here in this particular study, we synthesized novel metalloporphyrazine containing thio-ether linked 1,3-alternate calix[4]arene derivative and investigated their extraction selectivity for some transition metal cations.

2. Experimental

Unless otherwise stated, all operations were carried out under argon atmosphere in a vacuum line or using standard Schlenk techniques. The 25,27-bis(5-chloro-3-oxapentyloxy) calix[4]arene [20] and cis-1,2-dicyano-1,2-ethylenedithiolate [21] were prepared according to the methods described in the literature. All solvents were freshly purified by standard procedures before use [22]. ^{1}H and ^{13}C NMR spectra were measured on Varian Mercury 200-NMR and Varian Mercury Plus 300-MHz instruments. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer as KBr pellets. Mass spectra measured on micrOTOF and Micromass Quattro Ultima LC-MS/MS instruments. Electronic spectra were determined on a Shimadzu UV-1601 spectrophotometer which is double-beamed with thermostatically controlled cell block. The elemental analysis was performed on a Costech ECS 4010 instrument. Melting points were determined on an electrothermal apparatus and are uncorrected.

2.1. Synthesis of 1,3-alternate 26,28-bis[2-(2-iodoetoxy)etoxy]calix[4]arene-25-27-diol (*2*)

A solution of **1** (4.92 g, 7.72 mmol) in dry acetonitrile (150 ml) was added to a suspension of dry NaI (4.80 g, 32 mmol) in dry acetonitrile (50 ml) in a round-bottom two necked flask under argon atmosphere. The mixture was heated and stirred at reflux temperature for 7 days and monitored by a thin layer chromatography [silica gel (ethylacetate:hexane) (1:2)]. At the end of this period, the reaction mixture was cooled to room temperature, filtered to remove inorganic salt and washed with dry acetonitrile. The filtrate and wash solvent were combined and evaporated to dryness under reduced pressure. The crude product was dissolved in dry chloroform and filtered over Celite and then evaporated to dryness, yielding white solid that was purified by crystallization (chloroform:ethyl ether). Yield: 5.46 g (84.25%); mp. 176–178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 2H, -OH), 6.97 (d, 4H, ArH), 6.79 (t, 4H, ArH), 6.64 (m, 4H, ArH), 4.35(d, 4H, $ArCH_2Ar$), 4.10 (s, 4H, $ArCH_2Ar$), 3.96–3.89 (m, 8H, $ArOCH_2CH_2$), 3.32–3.26 (m, 8H, $ArOCH_2CH_2I$). ^{13}C NMR (75 MHz, $CDCl_3$): 153.18, 151.67, 133.30, 128.71, 125.44, 118.96. FT-IR (KBr pellets, cm^{-1}): 3340, 3028, 3016, 2921–2868, 1590, 1464, 1123–1033, 765. MS (ES): *m/z* 820 $[M]^{+}$, 838 $[M+H_2O]^{+}$. Anal. calcd. for $C_{36}H_{38}O_6I_2$:C, 52.68; H, 4.63. Found: C, 52,49; H, 4,86.

2.2. Synthesis of 1,3- alternate 26,28-[34,37-dithia-29,32,40,43-tetraoxa-35-en-carbodinitrile]calix[4]arene-25,27-diol (*4*)

A mixture of **2** (4.1 g, 5 mmol) and cis-1,2-dicyano-1,2-ethylene dithiolate (**3**) (0.93 g, 5 mmol) in dry acetonitrile (250 ml) was evacuated, refilled three times with argon and connected to vacuum line. The reaction mixture was refluxed and stirred vigorously under argon atmosphere for 6 days. At the end of this period, the mixture was cooled to room temperature and filtered off, washed with dry acetonitrile and then evaporated to dryness under reduced pressure. The yellow crude product was purified by using column chromatography [silica gel (chloroform)] to provide pale yellow solid product. Yield: 1.0 g (28.0%); mp.137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61(2, 2H, –OH), 7.01 (d, 4H, ArH), 6.76 (d, 4H, ArH), 6.65 (m, 4H, ArH), 4.31 (d, 4H, $ArCH_2Ar$), 4.13 (d, 4H, $ArOCH_2CH_2$), 4.00 (m, 8H, $ArOCH_2CH_2$), 3.60 (m, 4H, OCH_2), 3.24 (m, 4H, SCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.42 (Ar_{ipso}), 134.38 (Ar_{orto}), 129.55 (Ar_{meta}), 128.45 (Ar_{para}) 119.61 (C=C), 111.85 (C≡N), 71.62–69.46 (CH_2O), 32.28 (CH_2S). FT-IR (KBr pellets, cm^{-1}): 3361,3035, 3019, 2924–2867, 2209, 1591, 1465, 1127–1036, 763. MS (ES): *m/z* 707 $[M+1]^{+}$. Anal. calcd. for $C_{40}H_{38}N_2O_6S_2$: C, 67.98; H, 5.38; N, 3.97. Found: C, 67.72; H, 5.50; N, 4.17.

2.3. Synthesis of magnesium porphyrazine (*MgPz*)

Magnesium turnings (0.037 g, 1.54 mmol) and small crystals of I_2 were added to dry *n*-butanol (18 ml) under argon atmosphere. The mixture was refluxed until the magnesium had completely reacted to form a suspension of magnesium butoxide at overnight. A solution of **4** (3.53 g, 5 mmol) in dry *n*-butanol (10 ml) was added to the refluxing suspension and refluxed for 12 h. The reaction was monitored by a thin layer chromatography. After this period, the crude product was filtered off while hot. The dark blue solid was purified by column chromatography technique [silica gel (chloroform:methanol) (99:1)]. Yield: 1.5 g (42.1%); mp >300 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.68 (s, 8H, OH), 7.17 (m, 16H, ArH), 6.96 (m, 16H, ArH), 6.81(m, 16H, ArH), 4.27 (m, 16H, $ArCH_2$ Ar), 4.08 (m, 16H, $ArOCH_2CH_2$), 3.90 (m, 32H, $ArOCH_2CH_2$), 3.32 (m, 16H, OCH_2), 3.21 (m, 16H, SCH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.42 (C=N), 151.97 (Ar_{ipso}), 133.56 (Ar_{orto}), 129.24 (Ar_{meta}), 128.78 (Ar_{para}), 71.89–68.11 (CH_2O), 31.39 (CH_2S). FT-IR (KBr pellets, cm^{-1}): 3355, 3061, 3013, 1629, 1591, 1464, 1114–1026, 760. UV–vis [chloroform, λ_{max}/nm ($\log \varepsilon$)]: 677 (4,02), 615 (3,62), 379 (4,07), 352 (4,08), 280 (4,32). MS (ES): *m/z* 2848 $[M]^{+}$, 2871 $[M+Na]^{+}$. Anal. calcd. for $C_{160}H_{152}N_8O_{24}S_8Mg$: C, 67.42; H, 5.34; N, 3.93. Found: C, 67.59; H, 5.45; N, 3.72.

2.4. Synthesis of metal-free porphyrazine (*H₂Pz*)

Magnesium porphyrazine (0.60 g, 0.21 mmol) was dissolved in minimum amount of trifluoroacetic acid (5 ml) and stirred at room temperature for 4 h. The dark blue solution was poured over ice and neutralized with aqueous ammonia (33%) and extracted with dichloromethane (3 × 30 ml). The organic phase was washed with water and dried over $MgSO_4$ and then evaporated to dryness under reduced pressure. The crude product purified by column chromatography [silica gel (chloroform:methanol) (95:5)] gave dark blue solid. Yield: 0.35 g (59.1%); mp >300 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.71 (s, 8H, OH), 7.17 (m 16H, ArH), 6.97–6.87 (m, 16H, ArH), 6.83–6.71 (m, 16H, ArH), 4.34 (m, 16H, $ArCH_2Ar$), 4.10 (m, 16H, $ArOCH_2$), 3.92 (m, 32H, $ArOCH_2CH_2$), 3.33–3.18 (m, 32H, $ArCH_2Ar$, $ArOCH_2$), –1.55 (s, 2H, NH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.02 (C=N), 150.44 (Ar_{ipso}), 132.82 (Ar_{orto}), 129.38 (Ar_{meta}), 127.94 (Ar_{para}), 70.12–68.82 (CH_2O), 30.4 (CH_2S). FT-IR (KBr pellets, cm^{-1}): 3357, 3029, 3018, 2923–2867, 1635, 1591, 1465, 1123–1020, 761. UV–vis [chloroform, λ_{max}/nm ($\log \varepsilon$)]: 713 (3,92), 642 (3,83), 497 (3,70), 347 (4,28), 283 (4,55). MS (ES): *m/z* 2843 $[M+H_2O-1]^{+}$, 2866 $[M+K+1]^{+}$. Anal. calcd for $C_{160}H_{154}N_8O_{24}S_8$: C, 67.94; H, 5.45; N, 3.96. Found: C, 67.70; H, 5.58; N, 4.22.

2.5. Solvent extraction

Picrate extraction experiments were performed following Pedersen's procedure [23]. About 10 cm^3 of 2.5×10^{-5} M aqueous picrate solution and 10 cm^3 of 1×10^{-4} M solution of ligand in CH_2Cl_2 were vigorously agitated in a stoppered plastic tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at 25 °C for 1 h, and finally left standing for an