Journal of Hazardous Materials 217–218 (2012) 171–176

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Synthesis of crescent aromatic oligoamides with preorganized chelating groups and their extraction towards transition metal ions

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ARTICLE INFO

Article history:
Received 1 December 2011
Received in revised form 11 February 2012
Accepted 5 March 2012
Available online 15 March 2012

Keywords:
Aromatic oligoamide
Solvent extraction
Hydrogen bonding
Transition metal ion

ABSTRACT

Three crescent aromatic oligoamides **1–3** with their backbones rigidified by intramolecular hydrogen bonds were designed and synthesized. The liquid–liquid extraction by these compounds has been investigated using UV–vis spectrometry towards Pb^{2+} picrate and some transition metal picrates including Ag^{+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} salts. The results revealed higher selectivity and efficiency towards Hg^{2+} over other metal cations; pentameric ligand **1** with six oxygen donor atoms provided the highest extractability of 83.3%, while dimeric ligand **3** extracted almost exclusively Hg^{2+}. The stoichiometry of the extracted complex between ligand **1** and Hg^{2+}, and the extraction constant ($\log K_{ex}$) were determined in solvent extraction.

1. Introduction

Aromatic oligoamide are low molecular weight compounds that could be prepared by one-step or multiple steps condensation of para- or meta-substituted aromatic diamines and diacids [1]. Despite the presence of amide linkage in these oligomers that contains potential chelating groups (C═O) for metal complexation, few reports are available in solvent extraction using these compounds for separation of metal ions and/or for the formation of metal complexes. Failure to have an appropriate arrangement of oxygen atoms and well-defined cavities may be responsible for the inefficiency of metal complexation and lack of extraction ability. In recent years, aromatic oligoamides with enforced conformation based on intramolecular hydrogen bonding have attracted much attention for the characteristic folding and potential applications [2–5]. Among them, a class of aromatic oligoamides with backbones preorganized by aid of intramolecular three-center hydrogen bonds has been reported [6–12]. The introduction of electron-donating groups to the ortho-position of aromatic diamines and diacids followed by stepwise synthesis based on standard peptide chemistry led to compounds with an enforced crescent conformation in solution, which is remarkably different from the linear or coil conformation of traditional aromatic oligoamides. The significance of intramolecular hydrogen bonding present in these compounds was also manifested by the formation of their corresponding aromatic oligoamide macrocycles [9–11]. Recently we reported on efficient extraction towards lanthanide and actinide elements using cycloaramides [13]. Inspired by complexation of open-chain crown ethers which revealed marked complexation towards metal ions [14,15] as their cyclic analogues [16,17], acyclic species of these shape-persistent oligoamide macrocycles are likely to function similarly in metal chelating.

Transition metal ions such as Hg^{2+}, Cd^{2+}, and Pb^{2+} represent a typical class of heavy metal ions that are generally considered to have deleterious effect upon human beings and biological systems [18]. Removal of these toxic metal ions, especially mercury as a highly dangerous element [19], aroused a broad interest in academic field for treating waste water [20–25]. Besides, separation of metallic species of a similar chemical nature from each other was also required by the applications in the field of metallurgy [26]. Solvent extraction is considered to be an effective and energy saving technique suitable for these purposes. Although various types of sulphur-, nitrogen- and oxygen-containing host molecules, such as calixarenes, crown ethers, 1,2,4-triazole derivatives, thiacrowns and their related macrocyclic compounds have been developed and utilized for the extraction of Hg^{2+} [27–30], design of new extractants, particularly, those with selectivity, is still highly demanding. So far, there has been no report on the use of aromatic oligoamides with their backbones rigidified by intramolecular hydrogen bonds for solvent extraction of transition metal ions. With our continued interest in these aromatic oligoamide compounds, we report herein

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doi:10.1016/j.jhazmat.2012.03.010

on the design and synthesis of three acyclic oligomers **1**–**3** including pentamer, trimer and dimer and the liquid–liquid extraction towards Pb^{2+} and some transition metal ions including Ag^{+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}.

2. Experimental

2.1. Materials and reagents

Compounds **4**, **7** and **9** were synthesized following the similar reported procedures [7,9]. Dichloromethane, picric acid, anhydrous Na_2SO_4, $Hg(NO_3)_2{\cdot}1/2H_2O$, $AgNO_3$, $Pb(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ were the analytical grade reagents and were purchased from Chengdu Kelong Chemical Factory. All other solvents and chemicals used for the synthesis were of reagent grade and used as received.

2.2. Instruments and apparatus

UV–vis spectra were measured by SHIMADZU UV-2350. ^{1}H NMR and ^{13}C spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz). Chemical shifts are reported in δ values in ppm and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, and m = multiplet. High resolution mass data were collected by WATERS Q-TOF Premier. $CDCl_3$ and CD_3CN were from Cambridge Isotope Laboratories (CIL).

2.3. Synthesis of aromatic oligoamides

2.3.1. N-ethyl-2,4-bis(2-ethylhexyloxy)-5-nitrobenzamide (**5**)

2,4-Bis(2-ethylhexyloxy)-5-nitrobenzoic acid **4** (2.00 g, 4.72 mmol) and oxalyl chloride (0.90 g, 7.08 mmol) were mixed in dry CH_2Cl_2 (60 mL). DMF (10 μL) was added followed by bringing the solution to reflux. When bubbling in solution ceased the solvent was evaporated in vacuo to provide a yellow oil, which was dissolved in dry CH_2Cl_2 (30 mL) and added dropwise to a mixture of the $EtNH_2{\cdot}HCl$ (2.31 g, 28.3 mmol) and Et_3N (3.82 g, 37.8 mmol) in CH_2Cl_2 (30 mL). The solution was stirred at room temperature under N_2 overnight. The organic layer was washed with water, diluted hydrochloric acid and water, respectively. After drying over anhydrous Na_2SO_4 and filtration, the solvent was removed to afford the crude product. Further purification by column chromatography (petroleum ether/ethyl acetate, v/v, 6/1) provided the product (2.01 g, 94.5%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (s, 1H, ArH), 7.61 (t, J = 4.8 Hz, 1H, NH), 6.51 (s, 1H, ArH), 4.10 (m, 2H, OCH_2), 4.02 (m, 2H, OCH_2), 3.49 (m, 2H, $NHCH_2$), 1.87–1.77 (m, 2H, CH), 1.58–1.45 (m, 8H, CH_2), 1.38–1.30 (m, 8H, CH_2), 1.24 (t, J = 7.3 Hz, 3H, $NHCH_2CH_3$), 1.02–0.90 (m, 12H, CH_3).

2.3.2. 5-amino-N-ethyl-2,4-bis(2-ethylhexyloxy)benzamide (**6**)

Compound **5** (1.00 g, 2.22 mmol) was hydrogenated under stirring in the presence of 20% Pd/C (0.20 g) in CH_2Cl_2 (30 mL) at room temperature overnight. The solution was filtered in darkness as fast as possible followed by immediate removal of the solvent in vacuo to afford a light yellow oil (0.84 g, 89.9%). The obtained product **6** was used for the immediate coupling reaction.

2.3.3. 5-(2,4-dimethoxy-5-nitrobenzamido)-N-ethyl-2,4-bis(2-ethylhexyloxy)benzamid (**8a**)

Compound **7** (477 mg, 1.94 mmol) was dissolved in dry CH_2Cl_2 (30 mL) and added dropwise into a CH_2Cl_2 solution (30 mL) containing compound **6** (839 mg, 2.00 mmol) and Et_3N (306 mg, 3.03 mmol). The reaction was stirred in darkness at room temperature overnight. The reaction mixture was washed with diluted hydrochloric acid and water. After drying over anhydrous Na_2SO_4 the organic layer was filtered. Removal of CH_2Cl_2 and recrystallization from methanol afforded a faint yellow solid (1.11 g, 87.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (s, 1H, NH), 8.96 (s, 1H, ArH), 8.74 (s, 1H, ArH), 7.64 (t, J = 5.3 Hz, 1H, NH), 6.29 (s, 1H, ArH), 6.26 (s, 1H, ArH), 4.12 (s, 3H, OCH_3), 3.92 (m, 2H, OCH_2), 3.83 (m, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.43 (m, 2H, $NHCH_2$), 1.83–1.68 (m, 2H, CH), 1.53–1.35 (m, 8H, CH_2), 1.34–1.24 (m, 8H, CH_2), 1.17 (t, J = 7.3 Hz, 3H, $NHCH_2CH_3$), 0.98–0.81 (m, 12H, CH_3). ESI-HRMS (m/z) calcd. For $C_{34}H_{51}N_3O_8$ $[M+H]^+$ 630.3754, $[M+Na]^+$ 652.3574; found $[M+H]^+$ 630.3747, $[M+Na]^+$ 652.3580.

2.3.4. 5-amino-N-(5-(ethylcarbamoyl)-2,4-bis(2-ethylhexyloxy)phenyl)-2,4-dimethoxybenzamide (**8b**)

Compound **8a** (1.00 g, 1.59 mmol) was hydrogenated under stirring in the presence of 20% Pd/C (0.20 g) in CH_2Cl_2 (30 mL) at room temperature overnight. The workup was the same as for compound **6**. A white solid (0.83 g, 87.2%) was obtained for immediate use for the following reaction.

2.3.5. 4,6-bis(2-ethylhexyloxy)isophthaloyl dichloride (**10**)

Compound **9** (312 mg, 0.74 mmol) and oxalyl chloride (281 mg, 2.22 mmol) were mixed in dry CH_2Cl_2 (60 mL). DMF (10 μL) was added followed by bringing the solution to reflux. When bubbling in solution ceased the solvent was evaporated in vacuo to provide a yellow oil **10** (324 mg, 95.5%). The obtained compound **10** was used for the immediate coupling reaction.

2.3.6. 5-amino-N-ethyl-2,4-dimethoxybenzamide (**11**)

Compound **7** (983 mg, 3.82 mmol) was reacted with $EtNH_2{\cdot}HCl$ (1.87 g, 22.9 mmol) in the presence of Et_3N (3.86 g, 38.2 mmol) in CH_2Cl_2 (60 mL), followed by hydrogenation with 20% Pd/C (194 mg) in CH_2Cl_2 (50 mL) to provide the product as a white solid (780 mg, 91.0%). The obtained compound **11** was used for the immediate coupling reaction.

2.3.7. N1,N3-bis(5-(5-(ethylcarbamoyl)-2,4-bis(2-ethylhexyloxy)phenylcarbamoyl)-2,4-dimethoxy-phenyl)-4,6-bis(2-ethylhexyloxy)isophthalamide (**1**)

Compound **10** (324 mg, 0.71 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and added dropwise into a CH_2Cl_2 solution (40 mL) containing **8b** (831 mg, 1.38 mmol) and Et_3N (224 mg, 2.22 mmol). The reaction was stirred at room temperature overnight. The mixture was washed with diluted hydrochloric acid and water, dried over anhydrous Na_2SO_4 and filtered. Removal of CH_2Cl_2 and trituration of the crude product with methanol and ethyl acetate, respectively, afforded the product as a white solid (1.07 g, 91.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.60 (s, 2H, NH), 9.35 (s, 2H, NH), 9.06 (s, 2H, ArH), 8.97 (s, 1H, ArH), 8.92 (s, 2H, ArH), 7.66 (t, J = 5.2 Hz, 2H, NH), 6.48 (s, 2H, ArH), 6.44 (s, 3H, ArH), 4.06 (d, J = 5.8 Hz, 4H, OCH_2), 3.97 (s, 6H, OCH_3), 3.96 (s, 6H, OCH_3), 3.96–3.89 (m, 8H, OCH_2), 3.50 (m, 4H, $NHCH_2$), 1.84–1.74 (m, 6H, CH), 1.57–1.46 (m, 12H, CH_2), 1.46–1.40 (m, 12H, CH_2), 1.35–1.27 (m, 12H, CH_2 and m, 6H, $NHCH_2CH_3$), 1.25–1.21 (m, 12H, CH_2), 0.97 (t, J = 7.4, 6H, CH_3), 0.92 (t, J = 7.2, 18H, CH_3), 0.87–0.81 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.14, 162.70, 162.09, 160.01, 154.67, 153.85, 153.37, 151.98, 125.09, 122.20, 121.56, 114.26, 96.29, 95.01. ESI-HRMS (m/z) calcd. For $C_{92}H_{140}N_6O_{16}$ $[M+Na]^+$ 1608.0224; found $[M+Na]^+$ 1608.0267.

2.3.8. N1,N3-bis(5-(ethylcarbamoyl)-2,4-dimethoxyphenyl)-4,6-bis(2-ethylhexyloxy)isophthal-amide (**2**)

Compound **10** (590 mg, 1.28 mmol) was dissolved in dry CH_2Cl_2 (30 mL) and added dropwise into a CH_2Cl_2 solution (30 mL) containing **11** (560 mg, 2.50 mmol) and Et_3N (389 mg, 3.85 mmol). The reaction was stirred at room temperature overnight. After similar workup as for compound **1**, the residue was triturated with ethyl acetate to afford the product as a white solid **2** (0.96 g, 89.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.39 (s, 2H, NH), 9.03 (s, 1H, ArH), 8.90 (s, 2H, ArH), 7.49 (t, J = 5.4 Hz, 2H, NH), 6.47 (s, 1H, ArH), 6.44 (s, 2H, ArH), 4.08 (d, J = 5.6 Hz, 4H, OCH_2), 3.92 (s, 6H, OCH_3), 3.91 (s, 6H, OCH_3), 3.46 (m, 4H, $NHCH_2$), 1.90 (m, 2H, CH), 1.57–1.48 (m, 4H, CH_2), 1.43–1.38 (m, 4H, CH_2), 1.33–1.26 (m, 8H, CH_2), 1.21 (t, J = 7.2 Hz, 6H, $NHCH_2CH_3$), 0.93 (t, J = 7.4 Hz, 6H, CH_3), 0.85 (t, J = 6.9 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.00, 161.99, 160.05, 154.63, 152.50, 137.27, 125.05, 121.18, 115.28, 113.80, 96.41, 94.79. ESI-HRMS (m/z) calcd. For $C_{46}H_{66}N_4O_{10}$ $[M+H]^+$ 835.4857; found $[M+H]^+$ 835.4850.

2.3.9. 5-acetamido-N-(5-(ethylcarbamoyl)-2,4-bis(2-ethylhexyloxy)phenyl)-2,4-dimethoxybenz-amide (**3**)

Acetyl chloride (187 mg, 2.38 mmol) was added dropwise into a CH_2Cl_2 solution (50 mL) containing compound **8b** (857 mg, 1.43 mmol) and Et_3N (481 mg, 4.76 mmol). Following the same reaction condition and workup procedure similar to that of compound **2**, the product was obtained as a yellow solid (0.90 g, 88.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.57 (s, 1H, NH), 9.00 (s, 1H, ArH), 8.62 (s, 1H, ArH), 7.65 (t, J = 5.2 Hz, 1H, NH), 7.49 (s, 1H, NH), 6.37 (s, 1H, ArH), 6.35 (s, 1H, ArH), 3.91 (t, J = 4.0 Hz, 4H, CH_2), 3.86 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 3.41 (m, 2H, $NHCH_2$), 2.03 (s, 3H, $NHCOCH_3$), 1.71 (m, 2H, CH), 1.48–1.32 (m, 8H, CH_2), 1.27–1.18 (m, 8H, CH_2), 1.15 (t, J = 7.3 Hz, 3H, $NHCH_2CH_3$), 0.90 (t, J = 7.4 Hz, 3H, CH_3), 0.83 (t, J = 7.3 Hz, 6H, CH_3), 0.78 (t, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.90, 165.03, 162.60, 154.88, 154.00, 153.30, 152.09, 125.87, 125.50, 121.80, 121.10, 114.90, 114.37, 96.32, 95.15. ESI-HRMS (m/z) calcd. for $C_{36}H_{55}N_3O_7$ $[M+H]^+$ 642.4118, $[M+Na]^+$ 664.3938, $[M+K]^+$ 680.3677; found $[M+H]^+$ 642.4130, $[M+Na]^+$ 664.3907, $[M+K]^+$ 680.3663.

2.4. Transition metal extraction method

Pb^{2+} picrate and transition metal picrates including Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} were prepared by successive addition of a 1×10^{-2} M metal nitrate solution to 2×10^{-5} M aqueous picric acid solution and shaken at 25 °C for 1 h. Picrate extraction experiments were performed following Pedersen's procedure [31] using dichloromethane as organic phase. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction. 10 mL of a 2×10^{-5} M aqueous picrate solution and 10 mL of a 2×10^{-4} M solution of aromatic oligoamides in CH_2Cl_2 were put in a thermostated water bath at 25 °C and vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 h, then it was left standing for an additional 2 h to render two phases fully separate from each other. The concentration of the picrate anion remaining in the aqueous phase was determined by UV spectrophotometry at λ_{max} 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of ligands. The extractability of each metal by the ligands (E%) was calculated based on the equation: $E\% = 100(A_0 - A)/A_0$, where A_0 is the absorbance of the aqueous solution in the absence of ligand, A is the absorbance of the aqueous phase after extraction. Three independent experiments were carried out and the average value of percent picrate extracted was calculated.

3. Results and discussion

3.1. Synthesis and characterization

Typically aromatic oligoamides are synthesized based on the coupling reactions of acyl chloride and amine bearing alkoxy groups adjacent to carboxy or amino groups. Three crescent aromatic oligoamides **1–3** were prepared as shown in Scheme 1. All of these compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

The key precursor **8a** was obtained by reaction of acyl chloride **7** and 5-amino-N-ethyl-2, 4-dialkoxybenzamide **6** (R= iso-octyl) in the presence of Et_3N in CH_2Cl_2 at room temperature. Compound **6** was readily prepared via two steps from compound **4** followed by hydrogenation of compound **5** with Pd/C as catalyst. Finally condensation of reduced dimer **8b** and diacid chloride of 4,6-dialkoxyisophthalic acid **10** afforded the desired pentameric product **1** in 91% yield. The patterns and chemical shifts for each amide proton of compounds **1–3** are the same or similar to those of the previously reported compounds [12,32], indicating the persistence of three center hydrogen bonds in these molecules. The ESI mass spectrum showed highly intense peaks at m/z: 1608.0267 $[M+Na]^+$ (calcd. 1608.0224 $[M+Na]^+$), corresponding to the presence of the pentameric species. The synthesis of trimer **2** was achieved in a similar fashion by coupling **10** and 5-amino-N-ethyl-2,4-dimethoxybenzamide **11** prepared from compound **7** in a yield of 90%. The reaction of **8b** and acetyl chloride in the presence of Et_3N provided dimer **3** in 88%. High resolution results of compounds **2** and **3** are in full agreement with the desired structures (see Supplementary materials).

It is noteworthy that all of the designed molecules examined in solvent extraction contain intramolecular hydrogen bonds, particularly three-center hydrogen bonds, which is the prerequisite for the backbone to persist in a crescent conformation in solution. The rigid frame also renders the preorganized oxygen atoms of the molecule point to the center, making it possible for complexation to occur.

3.2. Liquid–liquid extraction and selectivity

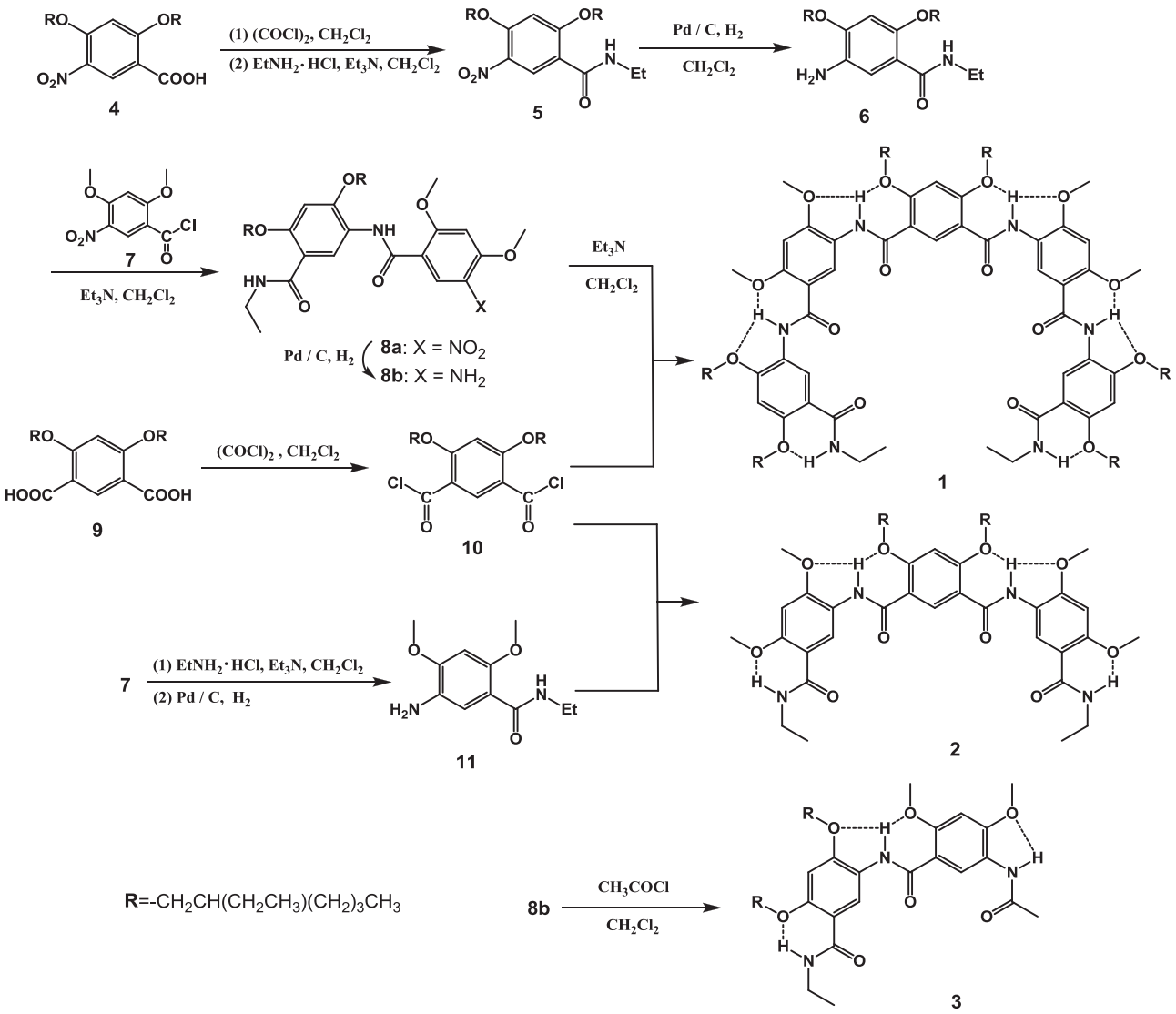
Pb^{2+} picrate and seven transition metal picrates including Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} salts were employed in liquid–liquid extraction experiments. The extraction abilities of aromatic oligoamides **1–3** towards these metal ions were examined by the standard picrate extraction method [33].

The extraction percentages are given in Table 1. Pentamer **1** showed extractability of 12–22% for most metal ions except for Ag^+ and Hg^{2+}. A moderate extractability of 35.1% was obtained for Ag^+. Interestingly, it extracted Hg^{2+} efficiently with the highest E% value of 83.3%. This indicated that this ligand is more selective towards

Table 1
The extractability of aqueous metal picrates for compounds **1**, **2** and **3** into dichloromethane.[a]

Metal ion	Extractability (%)[b]		
	Pentamer **1**	Trimer **2**	Dimer **3**
Hg^{2+}	83.3 ± 1.2	51.2 ± 0.9	46.4 ± 0.9
Ag^+	35.1 ± 0.1	7.4 ± 0.2	2.7 ± 0.7
Pb^{2+}	22.1 ± 0.5	6.5 ± 0.9	2.1 ± 0.7
Ni^{2+}	12.6 ± 0.2	6.7 ± 1.3	0.3 ± 0.4
Cd^{2+}	15.6 ± 0.4	6.6 ± 0.5	1.4 ± 0.2
Cu^{2+}	16.3 ± 0.4	6.5 ± 0.4	0.7 ± 0.2
Zn^{2+}	14.4 ± 0.7	4.5 ± 0.2	0.7 ± 0.2
Co^{2+}	14.3 ± 1.3	5.1 ± 0.5	0.3 ± 0.2

[a] Aqueous phase (10 mL); $[Pic^-] = 2 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 2 \times 10^{-4}$ M, 25 °C.
[b] Average for three independent extraction experiments.



Scheme 1. Synthesis of aromatic oligoamides **1–3**.

extracting Hg^{2+} than other metal cations. In the case of trimer **2** and dimer **3**, a similarly lower efficiency of extraction was observed for almost all the metal cations examined. The *E*% values for Ag^{+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Co^{2+} varied between 4.5% and 7.4% for **2**, and between 0.3% and 2.7% for **3**. In fact, this suggests almost lack of extraction towards these cations. The exception is the extraction for Hg^{2+}, which presented a much higher extractability of 51.3% for **2** and 46.4% for **3** over other cations. Thus, in all three cases of **1–3**, the selectivity for mercury is the highest compared to that for other metal cations. Since the number of internal carbonyl oxygens as chelating sites is in the order: **1** (six) > **2** (four) > **3** (three), the above results suggest the importance of coordinated oxygen atoms in extraction of mercury.

The binding properties of these aromatic oligoamides with structural similarity to open-chain crown ethers in terms of chelating sites should depend not only upon factors such as the hard and soft acids and bases (HSAB) principles, the type and number of donor atoms, but upon the cavity size, and orientation of donating atoms as well. It is known that ionic radii of the metal ions decrease in order of $Pb^{2+} > Ag^{+} > Hg^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ [34]; however, the observed extraction ability of oligomers **1–3** varied as $Hg^{2+} > Ag^{+} > Pb^{2+} > Cu^{2+} > Cd^{2+} \sim Zn^{2+} \sim Co^{2+} > Ni^{2+}$ for **1**, and $Hg^{2+} \gg Ag^{+}$ and other metal cations for **2** and **3**. Therefore, the size of these ligands does not fit well to accommodate metal ions, suggesting that the match between the above cations and the extractants is not the determinant for selectivity. Based on the above results, the high binding preference for Hg^{2+} is more likely to stem from the increased number of donor atoms in the ligands. However, since this failed to explain the small difference in extractability (4.8% per one donor atom increase) of mercury between **2** and **3**, and the large discrepancy (32.1% per two donor atoms increase) between **1** and **2** or that between **1** and **3** (36.9% per three donor atoms increase), other factors such as ion-pair induced self-assembly [35,36] of **1** or favorable geometrical arrangement upon complexing [37,38] may also play a role during solvent extraction.

To understand the complexing behavior of extracted species in solvent extraction, the complex stoichiometry of ligand and metal cations was determined. As shown in Fig. 1, the evolution of $\log\{D/[Pic^{-}]^{n}\}$ upon increasing the concentration of ligand **1** at constant Hg–picrate concentration led to a linear relationship between $\log\{D/[Pic^{-}]^{n}\}$ and $\log[L]$. The slope of the line was found to be 0.80 for pentamer **1**, suggesting the presence of the extracted species in approximately 1:1 (L:M) between **1** and Hg^{2+}. The extraction constant $\log K_{ex}$ value was determined to be 10.20. However, processing data as above failed to offer a linear relationship for trimer **2** and dimer **3**, making it impossible to calculate their

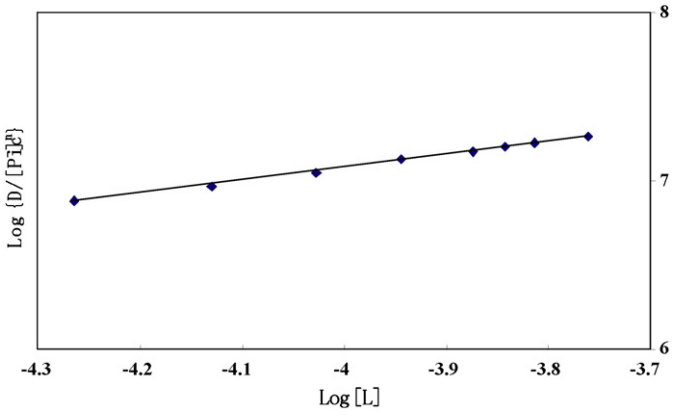


Fig. 1. Log $\{D/[Pic^-]^n\}$ versus log [L] for the extraction of Hg-picrate with pentamer **1**.

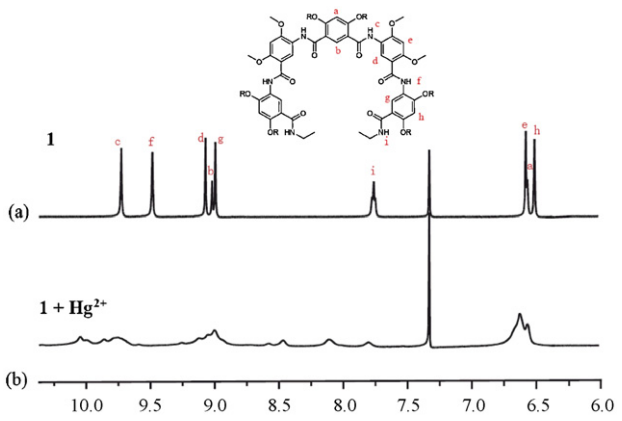


Fig. 2. Partial ^{1}H NMR spectra in 90%$CDCl_3$/10%CD_3CN. (a) **1** at 10 mM; (b) **1a** + $Hg(NO_3)_2$ (1:1) at 10 mM.

complex composition of extracted species and log K_{ex} values for Hg^{2+}.

In addition, the complexation of **1** with Hg^{2+} was examined in $CDCl_3/CD_3CN$ (v/v, 9/1) by ^{1}H NMR experiments. As shown in Fig. 2, the signals from both amide protons (**c**, **f**) and interior aromatic protons (**b**, **d**, **g**) turned broad upon addition of $Hg(NO_3)_2$, making them indistinguishable from each other in the region of 7.5–11 ppm. The exterior aromatic protons (**a**, **e**, **h**) experienced the same change in signal broadening, but remained almost unchanged in chemical shifts around 6.6 ppm compared to the free ligand **1**. This result indicated that the complexation of pentamer **1** with mercury ion did occur by aid of its internal carbonyl oxygens in the molecule, which explained the efficient extraction towards mercury.

4. Conclusion

In summary, three aromatic oligoamides with crescent backbone enforced via intramolecular three-center hydrogen bonds and conventional hydrogen bonds were designed and synthesized for liquid–liquid extraction towards Pb^{2+} and transition metal picrates. The results disclosed the higher selectivity and efficiency towards Hg^{2+} over other metal cations. In general, the oligoamide with more oxygen donor atoms provided a higher extractability in solvent extraction. Pentamer **1** stood out with the highest *E*% value of 83.3%, while dimer **3** extracted almost exclusively Hg^{2+} compared to other ions. The extraction ability was manifested by the importance of number of carbonyl oxygens in the constructed molecule, and geometrical arrangement of introverted donor atoms, which is realized by hydrogen bonding-enforced backbone rigidification. The selectivity observed in these ligands makes them potentially useful in separation of Hg^{2+} from other transition metal ions. In addition, the information retrieved from the present study will be beneficial to our further design of these backbone-rigidified aromatic oligoamides of various sizes for metal ion separation.

Acknowledgements

This work is supported by the National Natural Science Foundation (21172158), NSAF (11076018), the Doctoral Program of the Ministry of Education of China (20090181110047) and Open Project of State Key Laboratory of Supramolecular Structure and Materials (SKLSSM201112). Analytical & Testing Center of Sichuan University is acknowledged for NMR analyses.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.03.010.

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