Synthesis and characterization of Aza222-based polymers for the removal of mercury from aqueous solutions

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by

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Abstract

Polymeric materials for mercury complexation have been prepared by cross-linking 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane (H₆Aza222) with α,α' -dichloro-*p*-xylene and other multidentate electrophiles. Bulk and microporous *p*-xylyl-H₆Aza222 were shown to be effective at binding divalent mercury cations from aqueous solutions of HgCl₂ or Na₂HgI₄. The complexants were regenerable using solutions of HCl or Na₂S.

Introduction

Human activities annually emit over 100,000 kg of mercury into the environment. Coal-fired power plants account for the largest single percentage (nearly 50%, 48,000 kg/year) of this value.¹ Once released into the atmosphere, mercury in its various forms (elemental, inorganic salt or organic) is toxic. Between 1990 and 2012, world energy consumption increased from $3.54 \cdot 10^{17}$ to $5.42 \cdot 10^{17}$ Btu and is projected to increase to $7.7 \cdot 10^{17}$ Btu by 2035.² With the rising energy demand the number and output of coal-fired power plants must increase barring sudden and transformative growth in alternative technologies. It is thus critical that methods be developed to reduce emissions and to lower current environmental mercury levels.

A number of methods and materials for capturing mercury have been developed including microbial demercuration³, mercury adsorption on powdered activated carbon⁴ (which may be sulfur-impregnated for higher binding efficiency), precipitation of thiolates⁵ from aqueous solutions, reaction with thiol-modified mesoporous materials,^{6, 7} or capture with non-selective polymers such as synthetic ion-exchange,⁸ non-specific complexing materials,⁹ shredded tire rubber,¹⁰ or natural polymers such as animal wool.¹¹ Complex techniques utilizing more than one separation method or process have been studied as well.^{12, 13}

None of these methods, however, features a mercury sorbent that is simultaneously highly selective, high-capacity, regenerable and air-stable. For example, microbial

demercuration leads to reduction of the metal and formation of elemental mercury. In this state, the metal atoms may either agglomerate into mercury colloids or evaporate into the atmosphere, returning to the environment. Most ion exchange resins are not selective, and therefore require a large excess of the resin, especially since competing metals are often present in larger concentrations than mercury itself. The soft nature of mercury cations leads to their tendency to form stable complexes with polyamines and thiols. However, in many cases copper ions, which are more abundant than mercury in most natural aqueous systems, also form stable complexes with polyamines. Copper ions also catalyze the oxidation of thiols into disulfides reducing the mercury-binding ability of sulfur-containing materials. Sorbents such as finely shredded tire rubber, sulfur-doped activated carbon and wool can be used to decrease mercury concentrations in water 100 to 1000 fold, but have not proven to be regenerable. Since these materials are typically disposed of by combustion, the mercury is often re-released into the atmosphere.

The recent development¹⁴ of an easily-scaled synthesis of the complexant 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane, herein referred to as H₆Aza222 (Fig. 1), has opened up the possibility of building polymeric H₆Aza222-based resins for mercury binding.

[Figure 1]

Devices and processes based on those materials would be expected to outperform other methods for the following reasons:

- 1) Amines are much more resistant to oxidation than thiols or thioethers;
- 2) The H₆Aza222 cage geometry is optimal for binding mercury¹⁵ but not copper¹⁶ – a major natural mercury competitor for amine binding sites;
- 3) Regeneration of such materials could be accomplished by (a) rinsing with acid followed by deprotonation with base, (b) reaction with aqueous sulfides, or (c) reduction with NaBH₄ or H₂NNH₂;
- 4) In the course of regeneration, mercury could be recovered and contained in a concentrated form.

Experimental

Materials synthesis and properties.

Dicyclohexylmethanamine (Cy₂NMe) and α,α' -dichloro-*p*-xylene were purchased from TCI America; 2-(diisopropylamino)-ethanol, Celite-545, diisopropylethylamine, dimethylformamide (DMF) and dimethylacetamide (DMA) from Sigma-Aldrich; polyethylene glycol 20,000 (PEG) and K₂HgI₄ from Alfa Aesar; HgCl₂ from Baker Analyzed; sodium sulfide Na₂S·9H₂O (>98%) from Columbus Chemical Industries. All reagents were used as received.

Mercury concentrations were determined using flame atomic absorption (AA) measurements via a Varian SpectrAA-200 spectrophotometer. CHN/O analysis was performed on Perkin Elmer Series II CHNS/O Analyzer 2400 and IR spectra were collected on a Mattson Galaxy FTIR 3000 spectrometer.

Synthesis of 2HgCl₂·H₆Aza222. A solution of H₆Aza222·4H₂O (0.442 g, 1 mmol) in 5 mL of absolute ethanol was added to a solution of HgCl₂ (0.543 g, 2 mmol) resulting in a suspension of white material. The suspension was stirred for 2 hrs at room temperature, and then filtered and rinsed on a filter with excess of ethanol. Yield: 0.77g (85%).

Analysis: Calcd for C₁₈H₄₂Cl₄Hg₂N₈: C-23.67%, H-4.63%, N-12.27%; found C-23.49%, H-4.46%, N-11.98%. All attempts to purify that compound by recrystallization and determine its structure by crystal X-ray diffractometry failed due to low solubility of the substance in all solvents tested.

Synthesis of $2\text{Hg}(\text{ClO}_4)_2 \cdot \text{H}_6\text{Aza222}$. $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (3.35 g, 7.39 mmol) was dissolved in 60 mL of absolute ethanol containing 0.3 mL acetic acid. To that flask a solution of $\text{H}_6\text{Aza222} \cdot 1.37 \text{H}_2\text{O}$ (1.24 g, 3.14 mmol) in 5 mL of absolute ethanol was added. The resulting suspension was stirred for 2 h, filtered, rinsed with absolute ethanol and dried on a filter to give $2\text{Hg}(\text{ClO}_4)_2 \cdot \text{H}_6\text{Aza222}$. Yield: 2.64 g (72% based on $\text{H}_6\text{Aza222}$). Calcd for $\text{C}_{18}\text{H}_{42}\text{Cl}_4\text{Hg}_2\text{N}_8\text{O}_{16}$: C 18.49%, H 3.62%, N 9.58%, found: C 18.33%, H 3.56%, N 9.41%). Since the product tended to slowly decompose in refluxing ethanol, it was not recrystallized.

Determination of the $[\text{Hg}@\text{H}_6\text{Aza222}]^{2+}$ stability constant. $\text{H}_6\text{Aza222}$ was prepared according to the published procedure.¹⁴ $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (99%, Alfa Aesar) and 1.000 M HClO_4 (Riedel-de-Haën) were used for the synthesis of $\text{H}_6\text{Aza222} \cdot 2[\text{Hg}(\text{ClO}_4)_2]$ and determination of the $[\text{Hg}@\text{H}_6\text{Aza222}]^{2+}$ stability constant via a simplified version of a potentiometric titration. An Oakton pH meter was used for the acidity measurements and the data were combined and analyzed using Microsoft Excel 2000 spreadsheet software.

Since classical potentiometric titration has been shown to be inadequate for the determination of this constant,¹⁷ a modified procedure was used. A stock solution was prepared by placing 2.43 g $2\text{Hg}(\text{ClO}_4)_2 \cdot \text{H}_6\text{Aza222}$ into a mixture of 100 mL H_2O and 4.00 mL 1.000 M HClO_4 , which served to suppress the hydrolysis of Hg^{2+} cations and subsequent formation of insoluble HgO . Aliquots of 8 mL of that stock solution were placed into each of six 20 mL vials and the solution volume in each vial was brought to 10 mL by dilution with 0, 0.4, ..., 2 mL of 1.000 M HClO_4 and 2, 1.6, ..., 0 mL of 0.1 M NaClO_4 solution, which served as a supporting electrolyte. The change in concentration

of the supporting electrolyte from one solution to another was meant to compensate, at least partially, for the change in ionic strength due to multiple protonations of H₆Aza222. The vials were allowed to stand for 16 h and then the pcH (pcH = -log[H⁺]) values of their solutions were measured by a pH meter calibrated for pcH measurements of solutions with ionic strength 0.1 M at (20 ± 0.2) °C. That calibration was necessary because the proton activity was expected to differ significantly from 1 in the solutions with high ionic strength, so that the measured pH would not correspond to the proton concentration. The stability constant K_{HgL}:

$$K_{HgL} = \frac{[HgL^{2+}]}{[Hg^{2+}][L]} \quad (1)$$

was calculated according to the formula

$$K_{HgL} = \frac{([Hg^{2+}] + [HgL^{2+}]) \cdot \frac{\sum_{n=1}^6 nK_n[H^+]^n}{[HClO_4]_{add} - [H^+]} - 1 - \sum_{n=1}^6 K_n[H^+]^n}{[Hg^{2+}] + [HgL^{2+}] + 2 \frac{[HClO_4]_{add} - [H^+]}{\sum_{n=1}^6 nK_n[H^+]^n} (1 + \sum_{n=1}^6 K_n[H^+]^n)}, \quad (2)$$

where L signifies the non-protonated H₆Aza222 and K_n denotes the ligand's n^{th}

protonation constants $K_n = \frac{[H_nL^{n+}]}{[H^+]^n[L]}$ taken from the literature.²⁰

The equation for K_L assumed the existence of H₆Aza222 (denoted as L) in free and protonated forms H_nL^{n+} ($n=1$ to 6) and in the form of a ligand-mercury complex $Hg^{2+}L$. The possible existence of complexed protonated or hydrolyzed species or both (such as

HHgL³⁺ and HgOHL⁺) and influence of deviations of the ionic strength from 0.1 M on the stability constant were not considered.

Synthesis of bulk *p*-xylyl-H₆Aza222 polymer. H₆Aza222·4H₂O (0.42 g, 1 mmole), α,α'-dichloro-*p*-xylene (0.52 g, 3 mmol) and diisopropylethylamine ("Hunig's base" 0.78 g, 6 mmol) were dissolved in 5 mL DMF and kept at 160 °C for 30 min. The resulting resinous material was manually ground using a mortar and pestle, rinsed with water and dried. If the reaction took place according to the stoichiometry, 0.65 g of the polymer would have resulted. However, 1.23 g of the polymer was obtained, indicating that solvents and/or unreacted starting materials were trapped in the polymer product. This preliminary experiment demonstrated that polymerization was achieved and that the resulting resinous material displayed desirable mechanical properties for use in column and batch mercury adsorption experiments. Since the use of this bulk polymer in a column study proved unsuccessful due to poor feed flow through the material, further characterization of the bulk polymer was not performed and the synthesis of a microporous material was pursued.

Synthesis of microporous *p*-xylyl-H₆Aza222. A mixture of H₆Aza222·4H₂O (10.45 g, 23.6 mmol), α,α'-dichloro-*p*-xylene (12.41 g, 70.9 mmol), dicyclohexylmethylamine (30.00 g, 154 mmol) and polyethylene glycol (PEG) MW 20,000 (33.0 g) was placed into a 100 mL flask under a nitrogen atmosphere, stirred and heated to 120 °C to form a resin, and then held at this temperature for 20 min. The flask was cooled down to room temperature and the resin was broken into ~ 1 cm³ pieces. The resin chunks were further heated to 200 °C in the same flask for 30 min under nitrogen and then cooled to room

temperature for 3 h. The crude resin was removed from the flask, manually ground into 0.5 to 3 mm granules using a mortar and pestle, placed onto a fritted glass filter and washed with 200 mL isopropanol, 200 mL of deionized water, 500 mL 1M aqueous NaOH solution, 500 mL water, 200 mL isopropanol, and 200 mL hexane. The resulting product was dried on the fritted glass filter for 1 h and then kept under vacuum for 24 h. Yield: 9.18 g (57%). Calc. for $C_{42}H_{60}N_8$: C 74.51%, H 8.93%, N 16.55%. Found: C: 68.35%, H: 8.60%, N: 12.42%. These values indicated that the resin had a composition substantially different from what was expected, likely due to incomplete alkylation of some H₆Aza222 molecules, overalkylation of the others, and entrapment of some of the materials used in synthesis. Since PEG molecules could readily have been entangled or chemically attached to the Aza222 polymer as $-C_6H_4-CH_2-O-(CH_2CH_2O)_nH$ groups, they would not be removed by rinsing and vacuum drying. For a $C_{42}H_{60}N_8 \cdot 4.58(C_2H_4O)$ material, the calculated analysis is C 68.32%, H 8.78%, N 12.45%, which is much closer to the experimentally found values. A 1130 cm^{-1} band in the infrared spectrum is consistent with presence of PEG C-O ether bonds. IR (KBr pellet) $\nu = 3412$ (N-H stretch, O-H stretch), 2930 (C-H stretch), 2810 (C-H stretch), 1646 (N-H bend), 1457 (C-H, scissoring and bending), 1345 (C-N stretch), $1130\text{ (C-O stretch) cm}^{-1}$.

Preparation of poly[polyethylene imine/ α,α' -dichloro-*p*-xylene] polymer (PEI1) & (PEI2). To a 250 mL round bottom flask equipped with a magnetic stir bar and a reflux condensor, polyethyleneimine (21 g, 488 mmol monomer equivalents), polyethylene glycol (10 g), dicyclohexylmethylaniline (12.4 g, 63.5 mmol) and α,α' -dichloro-*p*-xylene (5.0 g, 28 mmol) were added. The solution was heated to 130°C and held at that temperature for 4 h (PEI2) or 24 h (PEI1). The resulting solid was cooled and rinsed

with 500 mL deionized water, 500 mL ethanol and 250 mL dichloromethane. Both resulting yellow solids were placed under vacuum at room temperature for 24 hrs. Yield: 8.6 g (**PEI1**), 4.3 g (**PEI2**). (**PEI1**): Anal. ($C_{20}H_{30}N_4Cl \bullet 3H_2O$); calcd C 57.74%, H 8.72%, N 13.47%, O 11.54%, Cl 8.52%; found C 58.63%, H 7.53%, N 12.72%. IR (KBr pellet) ν = 3450 (N-H, O-H), 2935 (C-H), 2796 (N-CH₂), 1654 (N-H). (**PEI2**): Anal. ($C_{12}H_{23}N_4 \bullet 1.25 H_2O$); calcd C 58.61%, H 10.45%, N 22.79%, O 8.13; found C 59.57%, H 10.22%, N 21.25%, O 8.96%. IR (KBr pellet) ν = 3450 (N-H, O-H), 3045 (C_{Ar}-H), 2953 (C-H), 1445 (C-H) cm⁻¹.

Column studies. The columns used for the initial studies were two custom-made glass tubes, ID=2.5 and 5 mm, 10 cm long, which narrowed at the bottom ($V \sim 0.5$ and 2 cm³). A 100 mL round flask with a 14/20 female joint was affixed on the top of the column for refilling the column. The bottom outlet was plugged with a glass wool plug, a short layer (ca. 3 mm) of clean sand and then a layer of Celite. In the thinner column described above, flow rates were low, so later studies employed the larger one.

Mercury absorption on bulk *p*-xylyl-H₆Aza222 polymer in column studies.

Initial experiments revealed that the dry polymer swells substantially upon wetting, so for column preparation, the polymer (0.80 g) was manually ground with mortar and pestle to ca. 0.2 mm particles, stirred as a suspension in water for 24 hrs, and then mixed up with Celite 545 (0.54 g, Sigma-Aldrich). The resulting suspension was poured into the 2 cm³ column and allowed to settle, yielding a material with manageable and consistent permeability. A solution of HgCl₂ (1.00 wt %, 240 mL) was then passed through, after which the column was rinsed with 640 mL deionized H₂O. Fifty-five 15 mL fractions of

the eluted solution were collected and evaluated for their mercury content via flame AA. Then, 100 mL of 1 M HCl followed by 400 mL H₂O were passed through the column and the concentration of mercury in the resulting eluent was determined.

Mercury absorption in a regenerable column. The 2 mL column was loaded with 66 mg of the microporous polymer (pre-wetted), and 5 mL aliquots of a 0.39% aqueous solution of HgCl₂, followed by variable volumes of saturated aqueous Na₂S were passed through in cycles. Water (~10 mL) was passed between mercury and sulfide washes to rinse out the excess of electrolytes and thus prevent formation of HgS precipitate from the cross-mixing. The eluted solutions were diluted to 100 mL in a volumetric flask and analyzed by flame AA. After the end of the experiment the resin was digested in aqua regia and analyzed for mercury content.

Column breakthrough. As described above, microporous polymer (62 mg) was ground with a mortar and pestle to ~ 0.2 mm particles, swelled in water for 24 hours, and mixed with 0.54 g Celite-545 (Sigma-Aldrich). The resulting suspension was loaded into the 2 mL column and allowed to settle. A solution of HgCl₂ (99 mg/250 mL, 396 ppm) was then passed through it in 10 mL portions. The eluent was collected in 20 mL vials and its mercury content was determined by flame AA.

Results and Discussion

Determination of Hg^{2+} -H₆Aza222 stability constant

Based on five measurements, the logarithm of the stability constant was found to be $\text{Log}K_L = 28.5 \pm 0.1$. To estimate the applicability of H₆Aza222-based resins for mercury removal in real systems and compare their performance with that of other immobilized ligands, one has to take into account competition phenomena that may negatively impact the formation of ligand-mercury complexes. Protonation and complexation of other metals may decrease the amount of ligand available for mercury binding, while hydrolysis and complexation reactions with other ligands may decrease the available concentration of mercury cations. Due to the many chemical species and processes involved, complete quantitative modeling of real systems may be unrealistic, but it is possible to estimate the performance of different ligands in systems where mercury binding competes with ligand protonation, copper complexation and hydrolysis. For that, a model comparing the ligands presented in Fig. 2 was developed.

Calculations on mercury complexation under competitive conditions

Limiting the set of species present in the solution to H^+ , OH^- , L, LH_n^{n+} , M^{2+} , MOH^+ and $\text{M}(\text{OH})_2$ ($\text{M}=\text{Cu}$ and Hg), the following equations can be written:

$$[M]_{\text{tot}} = [M^{2+}] + [\text{MOH}^+] + [\text{M}(\text{OH})_2] \quad (\text{M}=\text{Hg}, \text{Cu})$$

Here the concentrations of ML^{2+} are not shown as contributing to $[M]_{tot}$ because it is assumed that those complexed species are immobilized on the insoluble complexing resin.

[Figure 2]

Introduction of hydrolysis constants

$$K_{MOH} = \frac{[MOH^+]}{[M^{2+}][OH^-]} \quad (3)$$

and

$$K_{M(OH)_2} = \frac{[M(OH)_2]}{[M^{2+}][OH^-]^2} \quad (4)$$

allows for the expression of concentrations of the free metal ions as a function of the total metal concentration:

$$[M^{2+}] = \frac{[M]_{tot}}{1 + \frac{K_w}{[H^+]} \cdot K_{MOH} + \frac{K_w^2}{[H^+]^2} \cdot K_{M(OH)_2}} \quad (5)$$

If the total ligand concentration is defined as a sum of its neutral form and various protonated species and neglecting the HgL^{2+} complex (a reasonable approximation for the highly acidic solutions used for the stability constant determination):

$$[L]_{tot} = [L] + [L] \cdot K_1[H^+] + [L] \cdot K_2[H^+]^2 + \dots = [L] \cdot (1 + \sum_{n=1} K_n[H^+]^n) \quad (6)$$

a ligand concentration can be derived as a function of its total concentration:

$$[L] = \frac{[L]_{tot}}{1 + \sum_{n=1} K_n [H^+]^n} \quad (7)$$

Based on the definition of the stability constant

$$K_{ML} = \frac{[ML^{2+}]}{[M^{2+}][L]} \quad (8)$$

the concentration of the complexed species ML^{2+} can be expressed as

$$[ML^{2+}] = [M^{2+}][L] \cdot K_{ML} \quad (9)$$

Substitution of (5) and (7) into (9) yields

$$[ML^{2+}] = \frac{[L]_{tot}[M]_{tot} \cdot K_{ML}}{(1 + \sum_{n=1} K_n [H^+]^n) \left(1 + \frac{K_w}{[H^+]} \cdot K_{MOH} + \frac{K_w^2}{[H^+]^2} \cdot K_{M(OH)_2}\right)} \quad (10)$$

which allows an effective stability constant to be defined as

$$K_{ML}^{eff} = \frac{[ML^{2+}]}{[L]_{tot}[M]_{tot}} = \frac{K_{ML}}{(1 + \sum_{n=1} K_n [H^+]^n) \left(1 + \frac{K_w}{[H^+]} \cdot K_{MOH} + \frac{K_w^2}{[H^+]^2} \cdot K_{M(OH)_2}\right)} \quad (11)$$

The ligand selectivity factor

$$K_{Hg/Cu}^{sel} = \frac{[Hg^{2+}]}{[CuL^{2+}]} \cdot \frac{[Cu^{2+}]}{[Hg^{2+}]} \quad (12)$$

can be substituted by the effective selectivity factor defined here as

$$K_{Hg/Cu}^{eff,sel} = \frac{[Hg^{2+}]}{[CuL^{2+}]} \cdot \frac{[Cu^{2+}]_{tot}}{[Hg^{2+}]_{tot}} = \frac{K_{HgL}}{K_{CuL}} \cdot \frac{1 + \frac{K_w}{[H^+]} \cdot K_{CuH} + \frac{K_w^2}{[H^+]^2} \cdot K_{Cu(OH)_2}}{1 + \frac{K_w}{[H^+]} \cdot K_{HgH} + \frac{K_w^2}{[H^+]^2} \cdot K_{Hg(OH)_2}} \quad (13)$$

To compare the performance of H₆Aza222 with that of other polyamines in the systems where metal ions (Hg²⁺ and Cu²⁺) would be prone to hydrolysis and amines would be protonated, K_{ML}^{eff} and $K_{Hg/Cu}^{eff,sel}$ were calculated for the pH range 0-14 for eighteen amines shown in Fig. 2. The K_{ML}^{eff} and $K_{Hg/Cu}^{eff,sel}$ values were calculated from the literature values of K_{MOH} , $K_{M(OH)_2}$ and amine protonation constants¹⁸; in those cases where several constants were reported, an average value was used. Log $K_{CuH_6Aza222}$ and H₆Aza222 protonation constants were taken from a separate publication¹⁸ and the Log $K_{HgH_6Aza222}$ value was obtained in the course of this work. The stability constants of L19-L25 were taken from the earlier publication¹⁹ where they were determined for 80%MeOH-20%H₂O solutions and used without adjustments to the aqueous solutions. It was assumed that the polythioethers were not protonated over the pH range considered. All significant figures were carried out through the whole calculation processes and then rounded to the first decimal place. No further error analysis was performed.

Table 1 displays the binding constants for Hg and Cu along with selectivities between these metals for the three ligands: L4, L7 and L18. Table 2 illustrates the effective selectivities computed using eq. (13), which accounts for pH, ligand protonation and metal hydrolysis. Ligands L4, L7 and L18 were selected to demonstrate the general

trends in changes of the effective stability constants as function of pH, and show the macrocyclic effects on those constants.

[Table 1]

[Table 2]

As a general rule, the value of K_{ML}^{eff} is always less than that of the stability constants K_{ML} . The effective stability constants reach their maximal values at pH close to 7 and decrease in both acidic and basic regions because of the amine protonation and metal hydrolysis, respectively. The $LogK_{Hg/L}^{eff}$ values taken over fifteen pH values reflect ligand performance in solutions of different acidities. The effective selectivity constant $LogK_{Hg/Cu}^{eff,sel}$ approaches the difference between logarithms of the stability constants of the corresponding mercury and copper complexes in acidic solutions, when concentrations of both metal ions far exceed those of their hydrolyzed forms. Since mercury hydrolyzes more easily than copper, those values decrease with increasing pH and finally level off at high pH, when the dominant process for metal complexation becomes

The difference between $LogK_{Hg/Cu}^{eff,sel}$ values for the low and high pH points is 8.2 and is independent of the ligand because it is determined by the hydrolysis constants of the metal ions.

To emphasize the importance of the polycyclic nature of H₆Aza222 to its complexing ability, it is instructive to compare the way two ligands – linear tetracoordinating L4 and cyclic tetracoordinating L7 – change their $\text{Log}K_{\text{HgL}}^{\text{eff}}$ with changing pH. The stability constants of both ligands are close ($\text{Log}K_{\text{HgL}} = 25.0$ and 25.5) so that their $\text{Log}K_{\text{HgL}}^{\text{eff}}$ differ by only 0.5 at high pH values. As the solutions become more acidic, the concentration of free L7 decreases faster than that of L4 because L7 initially gets protonated more easily than L4 (protonation constants for L4: $\text{Log}\beta_1=9.8$ and $\text{Log}\beta_2=9.15$; for L7: $\text{Log}\beta_1=10.97$ and $\text{Log}\beta_2=9.87$). As a result, the effective stability constant for L4 exceeds that of L7 in the pH interval 10 to 6. However, when the pH decreases even further, the effective stability constants reverse again. The driving force for this process is the protonation of the additional nitrogens in L4 ($\text{Log}\beta_3=6.7$ and $\text{Log}\beta_4=3.48$) which is helped by the ligand's unfolding process that increases the distance between positive charges and thus allows more protons to bind to the amine sites. This unfolding cannot happen in L7, so its last two protonation constants ($\text{Log}\beta_3=1.6$ and $\text{Log}\beta_4=0.8$) are far lower than those of L4. As a consequence, at lower pH values, L7 is a much better ligand than L4. Generally speaking, one may assume that an increase in the number of rings in a polyamine ligand will likely increase its effective stability constant. That notion may be used as a guide for the syntheses of ligands exhibiting even greater binding strength than H₆Aza222.

The sum of $\text{Log}K_{\text{Hg}L}^{\text{eff}}$ values over the full pH range can serve as an aggregate measure of the efficiency of a given ligand's binding ability (Table 3.) The value for H₆Aza222 (L18) is exceeded by the corresponding values of the amines 6, 7, 13, 14, and 16, closely matches that of L10 and is approached by ligands 4, 5, 9 and 15. Out of that list only amines 4 and 6 are available commercially at a reasonable price, amine 5 is somewhat expensive and the other amines are either too expensive or are not available commercially. These results indicate that amines 4 and 6 would be ideal precursors for the synthesis of chelating resins for mercury sequestration where competition from other ions is minimal.

As with the summed binding ability, the sum ($\sum_{\text{pH}=0}^{14} \text{Log}K_{\text{Hg/Cu}}^{\text{eff,sel}}$) of the $\text{Log}K_{\text{Hg/Cu}}^{\text{eff,sel}}$ values as a function of pH represents the ligand's preference for mercury vs. copper over a broad pH range. Table 3 also shows sums of $\text{Log}K_{\text{Hg/Cu}}^{\text{eff,sel}}$ values for the eighteen ligands over fifteen pH values. Its value for H₆Aza222 (82.9) far exceeds that of the second best ligands L9 and L16, demonstrating that H₆Aza222 clearly outperforms other polyamines in its selectivity for mercury cations.

[Table 3]

The National Primary Drinking Water Regulations enforced by the U.S. Environmental Protection Agency define maximum contaminant levels (MCLs) for copper and mercury to be 1.3 mg/L (or $2 \cdot 10^{-5}$ M) and 0.002 mg/L ($1 \cdot 10^{-8}$ M), correspondingly. This means that in order to reduce the mercury concentration to levels below its MCL ($1 \cdot 10^{-8}$ M) in a

solution that already has copper at its MCL ($2 \cdot 10^{-5}$ M), the logarithm of the effective selectivity constant $\text{Log}K_{\text{Hg/Cu}}^{\text{eff,sel}}$ of the corresponding ligand should exceed

$$\text{Log} \frac{2 \cdot 10^{-5}}{10^{-8}} = 3.3.$$

As one can see from the Table 3, the corresponding pH value for

H₆Aza222 is 7; at pH=8 the $\text{Log}K_{\text{Hg/Cu}}^{\text{eff,sel}}$ becomes equal to 2.4 which, within this model, predicts that the H₆Aza222-based resin can bring down mercury concentration to that enforced by EPA at pH≤7. The last column in Table 3 shows the highest pH values at which the $\text{Log}K_{\text{Hg/Cu}}^{\text{eff,sel}}$ values of the corresponding ligands still exceed 3.3; H₆Aza222 (L18) clearly leads, and is followed by L5 (commercially available, but still costly) and commercially unavailable L9 and L16.

To compare polyamines with polythioethers, a data treatment like that above was performed for ligands L19 – L25 (Table 4). Since the stability constants of the corresponding copper complexes were unavailable, only the effective stability constants were calculated and compared with those of H₆Aza222.

[Table 4]

The first obvious difference between H₆Aza222 and polythioethers is the magnitude of the stability constant of their mercury complexes: $\text{Log } K_{\text{HgL}} = 28.5$ for H₆Aza222 vs. 12.0 for L12. However, the large value of this constant allows polyamines to bind mercury more efficiently than the polythioethers only in neutral and alkaline solutions, where

substantial amounts of the polyamine are present in their non-protonated form. In contrast, the effective stability constants of polythioethers with mercury decrease with increasing pH because hydroxide ions win the competition for mercury cations over the ligands under those conditions. That conclusion is in accordance with the reported ability of Mercaptoplex (a commercially available polymer that consists of polythioether groups connected to a polymeric backbone) to absorb Hg^{2+} cations in the 1.5-7.0 pH range¹⁵. Ultimately, when polyamines become virtually completely deprotonated (pH=14), the differences between the logs of the effective stability constants of all ligands in this study approaches the differences between the logs of the stability constants of the corresponding mercury complexes. The effective stability constants for H₆Aza222 and L24 match in the pH region 4-5, which means that polythioethers would be preferred materials for mercury removal from acidic solutions, while polyamines would absorb mercury more efficiently in neutral and basic solutions. This consideration gives insight into synthetic approaches to a ligand capable of effective mercury binding over a wider range of solutions: such a ligand should possess a linear polythioether chain connected to a macrocyclic polyazaligand.

This analysis demonstrates both the high stability of the Hg^{2+} ·H₆Aza222 complex and the much greater selectivity, compared to other amines, of H₆Aza222 for mercury vs. copper. Experiments on Aza222-based polymeric colloid (vide infra) do demonstrate its higher affinity for Hg^{2+} than for Cu^{2+} ions.²⁰ At the same time it illustrates that no single ligand can offer the highest stability constant value and the highest effective Hg/Cu selectivity ratio at all pHs.

Synthesis and characterization of H₆Aza222-based polymers

Reaction of H₆Aza222 with 1,2-dibromoethane performed in DMF in the presence of non-nucleophilic bases never yielded polymers. Only mixtures of various substituted amines were identified among the products. It is worth mentioning that the only well-defined product ever isolated from a similar reaction mixture (H₆Aza222 + 1,2-dibromoethane + K₂CO₃ in MeCN) in a low yield was the one shown on Fig. 3, a compound whose structure was determined by X-ray analysis .

[Figure 3]

[Scheme 1]

Polymers of different physical and chemical properties were made by reaction of H₆Aza222 with various cross-linking agents. These reactions are illustrated in Scheme 1. Reaction with XCH₂(-CH₂OCH₂)_nCH₂X, X=Cl, I, OTs, n=1-3, yielded gels of mechanical strength that were deemed insufficient for mercury absorption experiments. Complexing polymer suspensions were prepared by reaction of divinylsulfone (DVS) with H₆Aza222 at room temperature or below in protic solvents and used in the initial mercury absorption experiments. However, these DVS-H₆Aza222 resins were useless for

this project because of their solubility in acids, even as weak as acetic acid, so the search for more robust polymers was continued until polymers with the desired properties were found among reaction products obtained by reaction of H₆Aza222 with ClCH₂-*p*-C₆H₄-CH₂Cl and (ClCH₂-*p*-C₆H₄-)₂ in dimethylformamide (DMF), dimethylacetamide (DMA), benzonitrile, and decalin at T=100-220 °C. To bind the hydrogen chloride released in the course of alkylation, the additional bases (iPr)₂NEt (Hunig's base), (iPr)₂NCH₂CH₂OH and Cy₂NMe were employed. Of these bases, dicyclohexylmethylamine was found to be optimal because Hunig's base was too volatile (b.p.=127 °C) and (iPr)₂NCH₂CH₂OH was found to react with α,α'-dichloro-*p*-xylene at elevated temperature, probably via

alkylation of the hydroxyl groups. Reaction of H₆Aza222 with a 25% aqueous solution of sodium vinylsulfonate in 1:2 molar ratio followed by cross-linking of the resulting compounds (NaO₃S-CH₂CH₂-)_nH_{6-n}Aza222 by heating with (ClCH₂-*p*-C₆H₄-)₂ yielded a polymer containing negatively charged ethylene sulfonate groups, as indicated by IR.

Dropwise addition of a solution of H₆Aza222 and α,α-bis(tetramethylenesulfonium)-*p*-xyleneperchlorate (made by refluxing α,α-dichloro-*p*-xylene with tetrahydrothiophene and sodium perchlorate in acetonitrile) in *N*-methylpyrrolidone to hot (210 °C) mineral oil containing dicyclohexylmethylamine resulted in formation of small (~ 0.1 mm in diameter) polymer granules.

Scheme 2 shows the reaction of H₆Aza222 with α,α'-dichloro-*p*-xylene in the presence of dicyclohexylmethylamine, which yielded the most chemically stable and mechanically robust polymers. These preparations were used for the binding experiments.

[Scheme 2]

The 3412 cm^{-1} peak in the IR spectrum of the resin (Fig. 4) indicates the presence of N-H bonds. The fact that not all of the six N-H protons were replaced correlates well with the increasing difficulty of H₆Aza222 alkylation reactions as a function of the number of already substituted nitrogens. Thus, the reaction of H₆Aza222 with MeI proceeds¹⁵ only to the stage of formation of Me₄H₂Aza222; it is likely even more difficult for bulkier substituents to combine with the H₆Aza222 core. The difference between the theoretically calculated elemental composition of the polymer and that of the experimentally determined values corroborates the conclusion that the composition of the polymer is different from that of a stoichiometrically alkylated cage by α,α' -dichloro-*p*-xylene. Also the broad peak appearing at 837 cm^{-1} , typical for C-Cl bonds, suggests the presence of organic chlorine.

[Figure 4]

[Figure 5]

The microstructure of the resin revealed by SEM imaging (Fig. 5) shows that the sorbent consists of spherical particles that are ~ 1 micron in diameter agglomerated into a larger porous mass. The material's BET surface area ($3.6\text{ m}^2/\text{g}$) is consistent with a formulation of its structure as being composed of $1\text{ }\mu\text{m}$ particles that have $\sim 60\%$ of the surface exposed. We believe that the formation of the microstructure is caused by phase separation of the newly formed polymer from the polyethylene oxide.

Mercury absorption on bulk *p*-xylyl-H₆Aza222 polymer in column studies

Figure 6 illustrates that the concentration of HgCl₂ in the eluent continued to increase as the solution was passed through the column filled with bulk *p*-xylyl-Aza222. No well-defined breakthrough point was observed in this experiment, which can be explained by the slowness of diffusion of the HgCl₂ molecules into the bulk of the polymeric material leading to poor overall kinetics of binding. By the time the column was saturated, 0.45 g HgCl₂ was absorbed. This amount corresponds to 1.4 moles of mercury cations per mole of Aza222 ligand sites, assuming a resin composition of [(C₈H₈)₃Aza222]_n. The deviation of the amount of mercury absorbed over the expected value from the process described by the equation

indicates that other mechanisms for mercury binding could be involved. Most probable would be the complexation of the neutral HgCl₂ molecules with chloride anions resulting in formation of known complex anions HgCl₃⁻ and HgCl₄²⁻:

The complexation of chloride ions by HgCl_2 molecules ($\frac{[\text{HgCl}_3^-]}{[\text{HgCl}_2][\text{Cl}^-]} \approx 7$) and relatively low dissociation constant¹⁷ of HgCl_2 ($\frac{[\text{Hg}^{2+}][\text{Cl}^-]^2}{[\text{HgCl}_2]} = 10^{-13.5}$) support these hypotheses. This mechanism of complexation was corroborated by the composition of the complexes $2\text{HgX}_2 \cdot \text{H}_6\text{Aza222}$ ($\text{X}=\text{Cl}, \text{ClO}_4$) described above.

Physical dissolution of HgCl_2 in the resin material in a molecular form would increase the measured HgCl_2 uptake even more.

The weak binding of the mercury cations that are not trapped in Aza222 cages explains why a significant amount of HgCl_2 was removed by plain water rinsing. The total amount of HgCl_2 eluted with distilled water was found to be 262 mg leaving 188 mg HgCl_2 held strongly enough to withstand the column rinse (640 mL H_2O), which corresponds to filling of 59% of the binding sites of the resin. As Fig. 6 shows, mercury continued to be released from the resin even at the end of the water rinse, which indicates that even more mercury could have been released with subsequent rinsing. The additional rinse with 100 mL of 1M HCl followed by 400 mL H_2O released an additional 50 mg HgCl_2 , leaving 138 mg HgCl_2 on the column.

[Figure 6]

The coarse polymer clearly was able to retain mercury. However, it failed to demonstrate sharp saturation, efficiently retain a significant fraction of the absorbed Hg^{2+} cations, and undergo regeneration to a completely mercury-free form. The processes of both mercury absorption and desorption were sluggish. This can be explained by the slowness of

diffusion of mercury-containing species both in and out of the coarse material used to fill the column. This behavior contrasts with that of the microporous polymer described below.

A notable phenomenon that was observed was the slowing of the liquid flow during mercury absorption experiments. At the beginning of the experiment the flux was 0.85 cm³/min, and by the time the last portions of the solution were passed it had decreased to 0.012 cm³/min. This 70-fold flux decrease was ascribed to protracted resin expansion due to slow diffusion-based swelling (hydration), mercury chloride uptake or both.

Mercury absorption on a regenerable column

The concentration of mercury chloride in the stock solution was chosen to ensure that the amount of mercury added to the column (14.3 mg, 53 μmoles) stayed below the estimated capacity of the resin (~ 26.5 mg HgCl₂ or 19.6 mg Hg). To prevent possible HgS precipitation the amount of Na₂S in 5 mL of its saturated solution (~ 1g, ~13 mmoles) by far exceeded the amount necessary to bind mercury. Actually, precipitation of HgS in those experiments was never detected, suggesting that resin regeneration formed soluble species such as HgS₂²⁻, Hg₂S₃²⁻ and related anions that were subsequently washed out:

Based on the measured amounts of mercury in the eluted solutions, the amount of mercury remaining on the column was calculated and is presented in Table 5.

[Table 5]

The results demonstrate that the column absorbed virtually all the mercury salt that passed through it and decreased the metal concentration in the eluent to an undetectable level (<10 ppm). Also, they show that the column was regenerated with at least 50% efficiency with Na₂S solution in the intermediate cycles and that the regeneration was ~90% complete by the end of the last cycle. The measured mercury content in the resin by the end of the experiment was 1.6 mg, which correlated well with the value in Table 5 and showed that Na₂S was able to remove ~90% of the mercury from the column. This result demonstrates the regenerability of the Aza222-based resin as well as clear improvement of the performance of the microstructured resin over the coarse material.

Column breakthrough

To avoid column clogging, microporous *p*-xylyl-Aza222 resin (grain size 100 µm to 1 mm) was mixed with Celite-545 filler. As a result, the solution flux did not decrease to any notable extent throughout the whole experiment.

[Figure 7]

Figure 7 shows the mercury concentration in the eluent as a function of vial number. According to estimations (i.e. mass of the Aza222-resin and concentration of HgCl₂), a

1:1 Hg:Aza222 ratio corresponded to ~63 mL (6 vials) of the mercury solution. However, mercury concentration reached a detectable level (10 ppm) only after 140 mL of the feed solution was passed through the column. This implies that ~ 55% of the mercury cations were absorbed by a mechanism other than coordination by the polyazacages. The physical dissolution of mercury chloride in the resin and formation of tri- and tetrachloride anions of mercury are thought to be responsible for those findings. A control polymer was synthesized to ascertain whether this phenomenon was exclusive to the polyaza cage-based polymer. For the control, polyethylene imine (PEI), rather than the peraza[2.2.2] cryptand, was cross-linked using *p*-xylylene linkers (Scheme 3). Two batches (**PEI1** and **PEI2**) were synthesized with different cross-linking densities.

[Scheme 3]

Each polymer was subjected to a solution containing a high concentration of Hg^{2+} ions (~ 560 ppm) in the form of Na_2HgI_4 to compare the binding of each polymer to that of the cryptand-based polymer. Complexant **PEI1** performed quite well, sorbing 1.65 g Hg^{2+} /g polymer after 24 hours while **PEI2** performed poorly, only sorbing 77 mg Hg^{2+} /g. Assuming two Hg^{2+} ions per repeating unit, on a wt/wt basis as calculated for the Aza22 polymer, **PEI1** and **PEI2** should have binding capacities of 1.1 and 1.8 g Hg^{2+} /g respectively. Based on these estimated values, **PEI1** adsorbed 1.5 times as much as expected and **PEI2** adsorbed only ca. 4% of the expected amount. The difference in binding capability between **PEI1** and **PEI2** suggests that cross-linking density plays a significant role in Hg^{2+} binding, with higher cross-linking density resulting in much

higher Hg^{2+} binding. As in the case with the Aza222 polymer, this may be due to ion-pairing interactions between positively charged $[\text{N-Hg}]^+$ sites and the negatively charged HgI_4^{2-} from the feed. This may be much more prevalent in **PEI1** than **PEI2** since **PEI1** is more densely cross-linked and therefore there may be fewer free nitrogen binding sites adjacent to each other for $[\text{N-Hg-N}]$ binding to take place. Another possibility is that the presence of ‘dangling’ cross-linking units may play a role in binding.

The microstructure of the resin seemed to play a crucial role in making it different from the polymer formed in bulk synthesis. As seen in Fig. 7, there was no mercury detectable early in the column effluent (vials 1 through 14). Then its concentration rose slowly for the next 3 aliquots, then quickly to 50-85% of the initial mercury concentration. These data show that after the addition of ~ 51 mg of Hg^{2+} (4 times the expected capacity of the polymer on a weight basis), mercury was detected in the effluent, again suggesting the formation of tri- and tetrachloride anions of mercury.

Conclusions

The cage polyamine complexant $\text{H}_6\text{Aza222}$ was shown to demonstrate high affinity and selectivity for mercury cations. Microporous polymeric materials incorporating the complexant were prepared with α,α' -dichloro-*p*-xylene emerging as the cross-linking agent yielding materials with the best mechanical and chemical properties. Ion-exchange columns containing the resulting polymeric material were shown to absorb mercury from the solution. Regeneration and reuse of those materials has been demonstrated.

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Table 1. Stability constants and selectivities of mercury and copper complexation for three ligands

Ligand	L4		L7		L18	
LogK _{Hg} L	25.0	25.0	25.5	25.5	28.5	28.5
LogK _{Cu} L		20.1		24		18.1
LogK _{Hg/Cu} ^{sel}		4.9		1.5		10.4

Table 2. Calculated $\text{LogK}_{\text{HgL}}^{\text{eff}}$ and $\text{LogK}_{\text{Hg/Cu}}^{\text{eff,sel}}$ values for three ligands

	L4		L7		L18	
pH	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{Hg/Cu}}^{\text{eff,sel}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{Hg/Cu}}^{\text{eff,sel}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{Hg/Cu}}^{\text{eff,sel}}$
0	-4.1	4.9	2.2	1.5	-9.2	10.4
1	-0.1	4.9	5.8	1.5	-3.3	10.4
2	3.9	4.9	8.5	1.5	2.2	10.4
3	7.7	4.8	10.6	1.4	6.8	10.4
4	10.2	3.8	11.6	0.4	9.9	9.4
5	11.3	1.9	11.7	-1.5	11.9	7.4
6	12.3	-0.1	11.7	-3.5	13.5	5.4
7	12.9	-2.0	11.7	-5.4	14.5	3.5
8	13	-3.1	11.7	-6.6	15.2	2.4
9	12.8	-3.3	11.6	-6.7	15.3	2.2
10	11.8	-3.3	11.3	-6.7	14.8	2.2
11	10.0	-3.3	10.2	-6.7	13.4	2.2
12	8.0	-3.3	8.5	-6.7	11.5	2.2
13	6.0	-3.3	6.5	-6.7	9.5	2.2
14	4	-3.3	4.5	-6.7	7.5	2.2
$\sum_{\text{pH}=0}^{14} \text{LogK}$	119.7	0.2	138.1	-50.9	133.5	82.9

Table 3. Overview of ligand's mercury binding ability and selectivity over a broad pH range.

Ligand	LogK _{HgL}	LogK _{CuL}	$Log \frac{K_{HgL}}{K_{CuL}}$	$\sum_{pH=0}^{14} LogK_{HgL}^{eff}$	$\sum_{pH=0}^{14} LogK_{Hg / Cu}^{eff, sel}$	Max pH where $LogK_{Hg / Cu}^{eff, sel} \leq 3.3$
L1	8.8	4.2	4.6	-38	-4.9	4
L2	14.3	10.5	3.8	8.8	-16.9	3
L3	21.8	15.9	5.9	94.1	15.2	4
L4	25	20.1	4.9	119.7	0.2	4
L5	25.8	18.5	7.3	120	36.2	5
L6	27.7	22.8	4.9	138.6	0.2	4
L7	25.5	24	1.5	138.1	-50.9	-
L8	20.5	17.1	3.4	1.3	-21.7	3
L9	29.6	22.1	7.5	128.5	39.2	5
L10	25.3	29.1	-3.8	133	-130.3	-
L11	23	26.9	-3.9	84	-131	-
L12	23.7	24.4	-0.7	86.0	-83.8	-
L13	28.5	28.3	0.2	168.1	-70.3	-
L14	27.4	27.1	0.3	146.1	-68.8	-
L15	26.5	23.8	2.7	124	-32.8	-
L16	29.1	21.6	7.5	160.9	39.2	5
L17	17.9	15.7	2.2	59.0	-39.5	-
L18	28.5	18.1	10.4	133.5	82.9	7

Table 4. $\text{LogK}_{\text{HgL}}^{\text{eff}}$ of polythia- vs polyaza ligands at different pH.

	L19	L20	L21	L22	L23	L24	L25	L18
LogK_{HgL}	9.6	9.3	10.5	8.9	7.9	12.0	11.8	28.5
pH	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$	$\text{LogK}_{\text{HgL}}^{\text{eff}}$
0	9.6	9.3	10.5	8.9	7.9	12	11.8	-9.2
1	9.6	9.3	10.5	8.9	7.9	12	11.8	-3.3
2	9.6	9.3	10.5	8.9	7.9	12	11.8	2.2
3	9.5	9.3	10.4	8.8	7.8	11.9	11.8	6.8
4	8.5	8.3	9.4	7.8	6.8	10.9	11.7	9.9
5	6.6	6.3	7.5	5.9	4.9	9.0	8.8	11.9
6	4.6	4.3	5.5	3.9	2.9	7	6.8	13.5
7	2.6	2.3	3.5	1.9	0.9	5	4.8	14.5
8	0.6	0.3	1.5	-0.1	-1.1	3	2.8	15.2
9	-1.5	-1.7	-1	-2.1	-3.1	1	0.8	15.3
10	-3.5	-3.7	-3	-4.1	-5.1	-1	-1	14.8
11	-5.5	-5.7	-5	-6.1	-7.1	-3	-3	13.4
12	-7.5	-7.7	-7	-8.1	-9.1	-5	-5	11.5
13	-9.5	-9.7	-9	-10	-11.1	-7	-7	9.5
14	-11	-12	-11	-12	-13.1	-9	-9	7.5

Table 5. Column regeneration experiment. HgCl₂ feed solution concentration: 12.9 mM

Stage #	Step #	Comment	Hg in, mg	Hg out, mg	Hg column, mg
1					
	1	5 ml HgCl ₂ through	12.9±1.3	0	12.9±1.3
	2	H ₂ O rinse	0	0	12.9±1.3
	3,4	6 mL Na ₂ S+7 mL H ₂ O	0	9.7±1.0	3.2±1.6
2	1	5 ml HgCl ₂ through	12.9±1.3	0	16.1±2.1
	2	H ₂ O rinse	0	0	16.1±2.1
	3	5 mL Na ₂ S	0	10.6±1.0	5.5±2.3
	4	H ₂ O rinse	0	0.9±0.1	4.6±2.3
3	1	5 ml HgCl ₂ through	12.9±1.3	0	17.5±2.6
	2	H ₂ O rinse	0	0	17.5±2.6
	3	5 mL Na ₂ S	0	16±1.6	1.5±3.1
	4	H ₂ O rinse	0	0	1.5±3.1
4	1	5 ml HgCl ₂ through	12.9±1.3	0	14.4±3.4
	2	H ₂ O rinse	0	0	14.4±3.4
	3	Na ₂ S 5 mL	0	13.9±1.4	0.5±3.6
	4	H ₂ O rinse	0	0.4±0.04	0.1±3.6

Figure 1: Chemical structure of H₆Aza222.

Figure 2. Ligands used for stability constant and selectivity analysis.

Figure 3. Product obtained by using 1,2-dibromoethane for cross-linking of H₆Aza222.

Figure 4. IR Spectrum of the microstructured p-xylylene-Aza222 resin.

Figure 5. SEM images of complexing resin synthesized as shown in Scheme 2.

Figure 6. HgCl₂ absorption by p-xylyl-Aza222 column as a function of filtrate volume in mL.

Figure 7. Mercury concentration in effluent after passing 10 mL aliquots of a 396 mg/L HgCl_2 solution through a 2 mL column containing 63 mg of the microporous p-xylyl-Aza222 resin.

Scheme 1. Synthetic routes to various Aza222-based materials. RT – room temperature.

Scheme 2: Synthesis of complexing resin and theoretical product.

Scheme 3