



## Irreversible precipitation of mercury and lead

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### Abstract

There are immediate concerns with current commercial reagents that are used for heavy metal precipitation; in particular the fact that the reagents are not specifically designed to bind the targeted metals. The current literature reveals that not only do commercial reagents lack sufficient ability to strongly bind the metals, but they also fail to provide long-term stability as ligand–metal complexes under a variety of moderate conditions. For this reason a new ligand was designed and synthesized: 1,3-benzenediamidoethanethiol (BDETH<sub>2</sub>). It offers multiple, concerted, bonding sites for heavy metals and forms a stable metal–ligand precipitate. In this study, the formation of compounds comprised of this ligand with the divalent metals, lead and mercury, was explored and the pH stability of the water insoluble precipitates was determined. The leaching properties of the metal–ligand precipitates were determined using inductively coupled plasma (ICP) spectroscopy and cold vapor atomic fluorescence spectroscopy (CVAF). The results indicate that a 50.00 ppm lead solution at a pH of 4.0 may be reduced to a concentration of 0.05 ppm (99.9% lead removal) and to 0.13 ppm (99.7% lead removal) at a pH 6.0. A 50.00 ppm mercury solution at pH 4.0 may be reduced to a concentration of 0.02 ppm (99.97% mercury removal) and to 0.02 ppm (99.97% mercury removal) at a pH of 6.0. © 2001 Published by Elsevier Science B.V.

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### 1. Introduction

Heavy metal pollution is a worldwide problem that will continue to grow. Mercury and lead are two heavy metals that are abundant in the ecosystem of the earth, and available largely due to anthropogenic sources. It has been estimated that mercury emissions globally exceed 3000 tons annually [1]. The element can be found in air, sediments, soils, seawater, and fresh waters. Effects of the high levels of mercury in blood and hair can be correlated with sensory disturbances (paresthesia, hypaesthesia), constriction of the visual field, hearing

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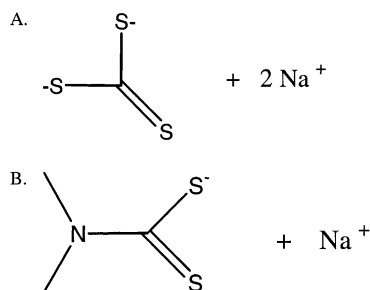
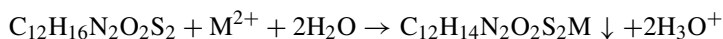


Fig. 1. Structures of current market metal chelating compounds. (A) STC (potassium/sodium thiocarbonate); (B) SDTC.

impairment, and neurological disturbances [2]. High levels of bioaccumulated mercury have also been detected in the United States, where several states have instituted warnings for fish consumption from state lakes and streams. Lead is also toxic with various detrimental biological effects including inhibition of the synthesis of hemoglobin [3], dysfunction in the kidneys, reproductive system, liver, and the central and peripheral nervous systems [4,5].

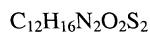
To protect the quality of surface and ground water from heavy metal pollutants, such as Cd, Cu, Pb, Hg, and Zn, federal and state governments have instituted environmental regulations [6]. In response to the regulatory requirements, numerous companies have marketed common reagents for the precipitation of heavy metals from wastewaters [7]. Examples of these reagents include sodium dimethyldithiocarbamate (SDTC) and sodium thiocarbonate (STC) (Fig. 1). Literature data on SDTC and STC have shown that the reagent–metal combinations can readily decompose into other substances, including HgS.

Previous laboratory experiments with the thiocarbamate and thiocarbonate compounds have shown that many of these compounds can decompose into hazardous materials during chelation, have high leaching rates, and are not effective at pH ranges less than 4.0 [1,7,8]. Additional concerns with compounds such as SDTC and STC include the weak bidentate binding abilities for heavy metals. For this reason, it has been the focus of our research to design and synthesize thiol-based compounds which maximize binding sites for heavy metals and result in stable precipitates. To produce stable precipitates, we have designed an economical 1,3-benzenediamidoethanethiol ligand (BDETH<sub>2</sub>) based on hard-soft acid–base (HSAB) interactions (Fig. 2) [9]. In general, the HSAB principle predicts that a soft base, such as disodium BDETH<sub>2</sub> (Fig. 2), should preferably interact and bond with soft metals, such as Hg<sup>2+</sup> and Pb<sup>2+</sup> [9]. Fig. 3 illustrates the type of complex, which results in a likely stable BDETH<sub>2</sub> complex with a divalent metal. The theoretical reaction, which produces the predicted stable precipitate is:



where M<sup>2+</sup>: Pb, Hg, Cd, Cu, Zn, etc.

The BDETH<sub>2</sub> has been characterized by proton and carbon nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR), infra-red spectroscopy (IR), mass spectrometry, X-ray diffraction (XRD), and carbon, hydrogen, nitrogen, and sulfur elemental analysis (CHNS-EA). Current research emphasizes interactions between the BDETH<sub>2</sub> ligand and mercury, cadmium,



Molecular Mass (grams): 284.07

Ideal Chemical Analysis (%): C, 50.68; H, 5.67; N, 9.85; O, 11.25; S, 22.55

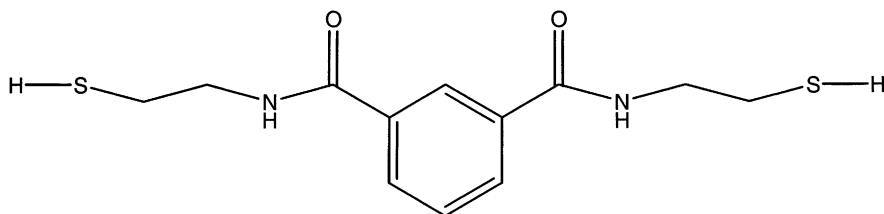


Fig. 2. Structure and chemical information of the BDETH<sub>2</sub> ligand. C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, molecular mass (grams): 284.07, ideal chemical analysis (%): C, 50.68; H, 5.67; N, 9.85; O, 11.25; S, 22.55.

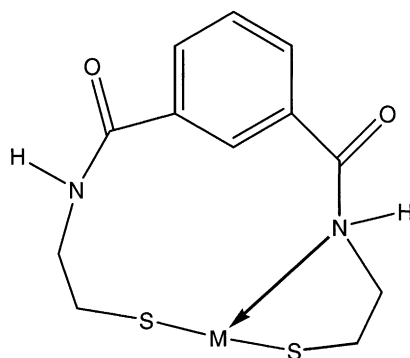


Fig. 3. Proposed structure of BDETH<sub>2</sub> ligand–metal complex.

copper, lead, and iron (II). This paper outlines the reactivity and stability of the BDETH<sub>2</sub> ligand with Pb<sup>2+</sup> and Hg<sup>2+</sup>.

## 2. Materials and methods

### 2.1. Materials

Synthesis of the BDETH<sub>2</sub> compound is a patent pending procedure and utilized the following reagent-grade materials: isophthaloyl dichloride (C<sub>8</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>, ACROS, lot no. A011508701) and cysteamine (C<sub>2</sub>H<sub>7</sub>NS, Fluka, lot no. 49087/1), triethylamine (C<sub>6</sub>H<sub>15</sub>N, Fischer, lot no. 001202), and dry HPLC grade chloroform was used as a reaction solvent

(CHCl<sub>3</sub>, Mallinckrodt, lot no. 4443N13H27). For the BDETH<sub>2</sub> ligand metal reactions, reagent-grade materials were also used, including lead acetate with three waters of hydration (PbC<sub>4</sub>H<sub>6</sub>O<sub>4</sub>·3H<sub>2</sub>O, Mallinckrodt, lot no. 5688N52585), and mercuric chloride (HgCl<sub>2</sub>, ACROS, lot no. B0100782). For reactions in a sodium acetate buffer solution, the buffer was prepared at pH 6.0 using sodium acetate (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O, J.T. Baker Inc., lot no. 744103), and glacial acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, Mallinckrodt, lot no. V193N08H38).

## 2.2. Analytical methods

Lead analyses were performed with a 1999 Duo HR Iris advanced inductive coupled plasma (ICP) spectrometer. Mercury results were obtained using cold vapor atomic fluorescence spectroscopy (CVAF) on a Varsal atomic fluorescence spectrometer, model number VI2000, using EPA techniques for mercury analyses [10]. For powder XRD analyses, the samples were mounted on glass slides with ethanol and analyzed with a Rigaku unit at 40 kV and 20 mA using Cu K $\alpha_1$  ( $\lambda = 1.540598 \text{ \AA}$ ) radiation. No pattern matches were obtained for the BDETH<sub>2</sub> ligand or metal–ligand complexes when compared with organic and inorganic databases from the International Centre for Diffraction Data (ICDD) (Newton Square, Pennsylvania). Proton and carbon NMR analyses were performed on a Varian–Gemini-400 instrument the samples were run in deuterated chloroform (CHCl<sub>3</sub>, Cambridge Isotope Laboratories) and deuterated dimethyl sulfoxide (C<sub>2</sub>H<sub>6</sub>SO, Cambridge Isotope Laboratories). Infrared spectroscopy data on the BDETH<sub>2</sub> ligand and the BDETH<sub>2</sub> ligand–metal complexes were collected as potassium bromide pellets using spectroscopy grade potassium bromide (KBr, Mallinckrodt, lot no. 0505 KXRX) using a Nicolet–Avatar 320 FT-IR series spectrometer. Elemental analyses were determined on a Vario Elementar III (Fig. 2). All masses were obtained with a Sartorius BP2100S or a Mettler AE 240 balance.

## 2.3. Analytical procedures for ICP analyses

### 2.3.1. Lead ICP analyses

A series of 100 ml 50.00 ppm Pb<sup>2+</sup> samples were prepared. A total of 0.0069 g of solid BDETH<sub>2</sub> ligand, based on a 1:1 metal to ligand mole ratio, was immediately added to the lead solutions. The reaction produced pH 4.0 solutions. Aliquots of 10 ml were collected and filtered at 0.2  $\mu\text{m}$  (Nalgene<sup>®</sup> syringe filters lot no. 322238) at 1, 6, and 20 h. The experiment was repeated using a 50.00 ppm solution with the addition of an acetic acid/sodium acetate buffer (5.0 ml) to maintain a pH of 6.0. Samples of 10 ml were collected and filtered using 0.2  $\mu\text{m}$  Nalgene<sup>®</sup> syringe filters at 2, 6, and 20 h. Each experiment was repeated for a minimum of four times and the final average values have been tabulated in Table 1 (Fig. 4).

### 2.3.2. Mercury cold vapor analyses

A 100 ml 50.00 ppm Hg<sup>2+</sup> sample was prepared as an aqueous solution, and 0.0071 g of solid BDETH<sub>2</sub>, based on a 1:1 metal to ligand mole ratio, was immediately added to the mercury solution. Three additional samples were prepared, one additional 1:1 mole metal to ligand ratio and two with ligand dosages 10% above the 1:1 molar ratio. A total of 5.0 ml of acetic acid/sodium acetate buffer were added to one of the 1:1 and to one of the 10% excess

Table 1  
ICP and CVAF results of BDETH<sub>2</sub> with Pb<sup>2+</sup> and Hg<sup>2+</sup>

Metal	Original metal conc. (ppm)	Ligand dosage (g)	Dosage increase as % of 1:1 molar ratio	Milliliter of added buffer <sup>a</sup>	Solution pH	Time (h)	Final metal conc. (ppm) <sup>b</sup>	Maximum % metal removal
Lead	50.00	0.0069	0.00	0.00	4.00	1	0.10	99.8
Lead	50.00	0.0069	0.00	0.00	4.00	6	0.05	99.9
Lead	50.00	0.0069	0.00	0.00	4.00	20	0.05	99.9
Lead	50.00	0.0069	0.00	5.00	6.00	1	0.31	99.4
Lead	50.00	0.0069	0.00	5.00	6.00	6	0.22	99.6
Lead	50.00	0.0069	0.00	5.00	6.00	20	0.13	99.7
Mercury	50.00	0.0071	0.00	0.00	4.00	1	1.96	96.09
Mercury	50.00	0.0071	0.00	0.00	4.00	6	1.65	96.71
Mercury	50.00	0.0071	0.00	0.00	4.00	20	0.93	98.14
Mercury	50.00	0.0071	0.00	5.00	6.00	1	0.50	99.01
Mercury	50.00	0.0071	0.00	5.00	6.00	6	0.13	99.74
Mercury	50.00	0.0071	0.00	5.00	6.00	20	0.09	99.81
Mercury	50.00	0.0078	10.00	0.00	4.00	1	0.58	98.85
Mercury	50.00	0.0078	10.00	0.00	4.00	6	0.39	99.22
Mercury	50.00	0.0078	10.00	0.00	4.00	20	0.02	99.97
Mercury	50.00	0.0078	10.00	5.00	6.00	1	0.31	99.39
Mercury	50.00	0.0078	10.00	5.00	6.00	6	0.06	99.89
Mercury	50.00	0.0078	10.00	5.00	6.00	20	0.02	99.97

<sup>a</sup> Buffer solution created from acetic acid and sodium acetate.

<sup>b</sup> Maximum percentage results are based on the average of four runs.

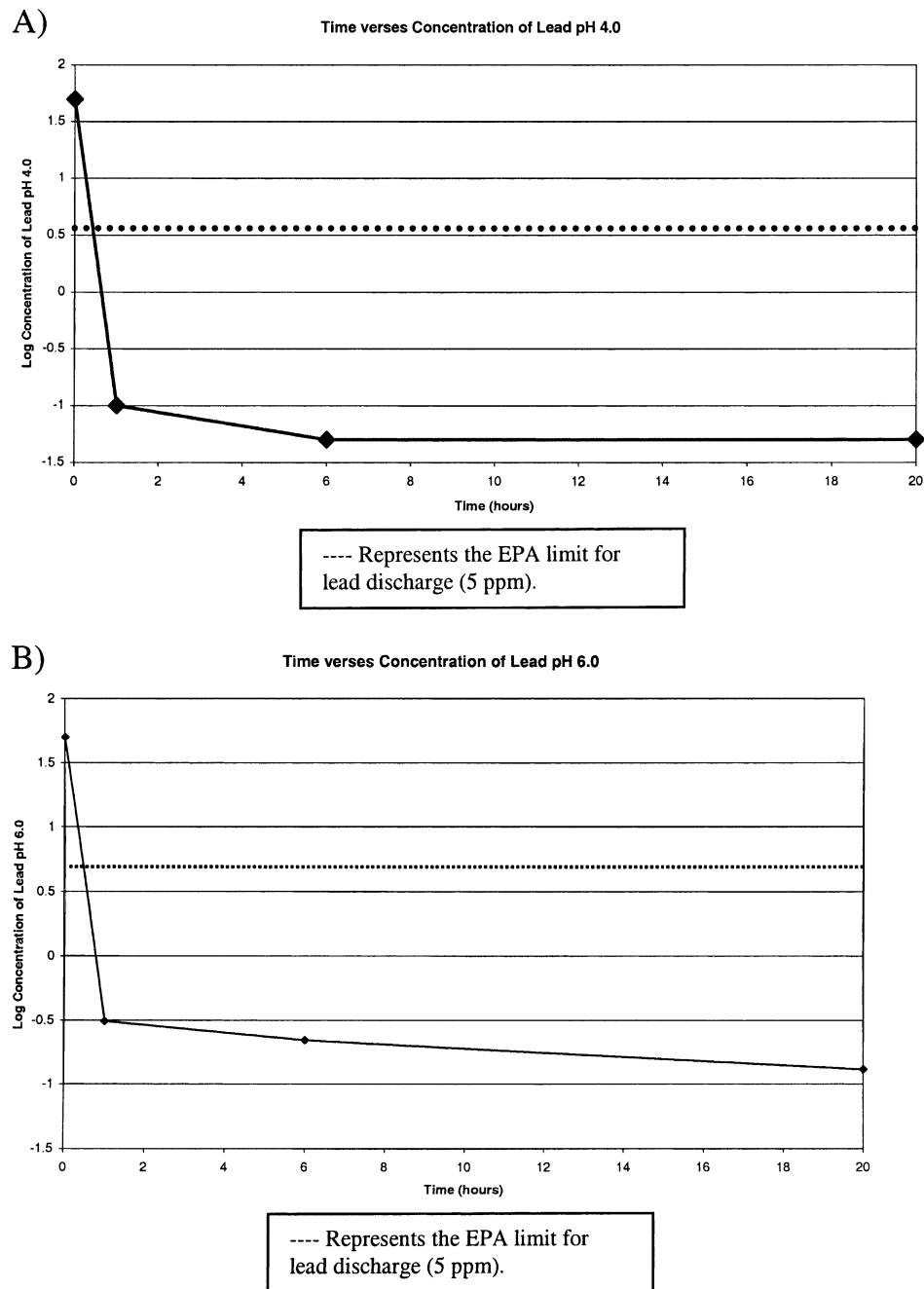


Fig. 4. Removal of lead at pH 4.0 and 6.0. (A) Removal of lead at pH 4.0 using a 1:1 molar dose of BDETH<sub>2</sub> ligand; (B) removal of lead at pH 6.0 using a 1:1 molar dose of BDETH<sub>2</sub> ligand.

samples to maintain a pH of 6.0. Samples of 10 ml were collected and filtered with 0.2  $\mu\text{m}$  Nalgene<sup>®</sup> syringe filters at 1, 6, and 20 h for each sample. Each experiment was repeated for a minimum of four times and the final average CVAF values have been tabulated in Table 1 (Fig. 5).

### 3. Results and discussion

#### 3.1. Characterization of precipitates

The ligand–metal complexes were analyzed with XRD, <sup>1</sup>H NMR, IR, and CHNS-EA. The XRD patterns of the recovered crystalline precipitates were compared using organic and inorganic databases from the International Centre for Diffraction Data (ICDD) (Newton Square, Pennsylvania). For the <sup>1</sup>H NMR analyses, the spectrum of the unbound BDETH<sub>2</sub> ligand was compared to that of the metal–ligand complexes. The spectrum for the BDETH<sub>2</sub> ligand yielded: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 1.44 (t, 2H), 2.90 (q, 4H), 3.71 (q, 4H), 7.56 (t, 1H), 7.98 (d, 2H), 8.21 (s, 1H) (Fig. 6). Two comparative <sup>1</sup>H NMRs were obtained in deuterated dimethylsulfoxide (DMSO) acidified with one drop of HNO<sub>3</sub> and a second in deuterated DMSO acidified with one drop of HCl. Acidified DMSO was used because of the insolubility of the ligand–metal complexes in organic and acidified aqueous solutions. Acidifying the DMSO–ligand–metal solution allowed for enough solubility to create a suitable solution for the <sup>1</sup>H NMR analyses. Peak splitting could not be identified due to the low concentration of the ligand–metal complexes; however, the spectrum did yield strong broad peaks that confirmed the presence of aromatic and alkane protons. The IR data confirmed the presence of the BDETH<sub>2</sub> major functional groups. The confirmed wavelengths of the functional groups included: secondary amine (–NH–) 3236.98 cm<sup>–1</sup>, aromatic (CH's) on the benzene ring 2924.61 cm<sup>–1</sup>, sulfur–hydrogen bond (S–H) 2555.90 cm<sup>–1</sup>, carbonyl (CO) 1639.26 cm<sup>–1</sup>, and the carbon–sulfur bond (C–S) 697.01 cm<sup>–1</sup> [11]. IR data on both of the metal complexes (Hg<sup>2+</sup> and Pb<sup>2+</sup>) confirm the carbonyl, the C–S bond, the aromatic CH's on the benzene ring, and the secondary amine peak [11]. The only missing peak in both complexes was the sulfur–hydrogen bond, which was replaced by the expected metal–sulfur bond. The metal–sulfur bond should be located at wavelengths below the Nicolet–Avatar 320 FT-IR series spectrometer's detection limit of 500 cm<sup>–1</sup> [12,13]. CHNS-EA for the BDETH<sub>2</sub>–mercury complex found C, 29.18%; H, 3.15%; N, 5.45%; S, 12.47% with calculated values of C, 29.84%; H, 2.92%; N, 5.80%; S, 13.28%. CHNS-EA for the BDETH<sub>2</sub>–lead complex found C, 28.77%; H, 2.88%; N, 5.50%; S, 13.02% with calculated values of C, 29.44%; H, 2.88%; N, 5.72%; S, 13.10%.

#### 3.2. Results of Pb<sup>2+</sup> and Hg<sup>2+</sup> stoichiometry and removal as determined from the ICP and CVAF data

ICP indicates a maximum Pb<sup>2+</sup> removal at 6 h for the 1:1 mole ratio at pH 4.0 (0.05 ppm 99.9%) (Table 1; Fig. 5). Maximum removal of Pb<sup>2+</sup> occurred at 20 h for the pH 6.0 solution (0.13 ppm, 99.7% removal) at a dosage of 1:1 mole lead to ligand ratio (Table 1; Fig. 4). It

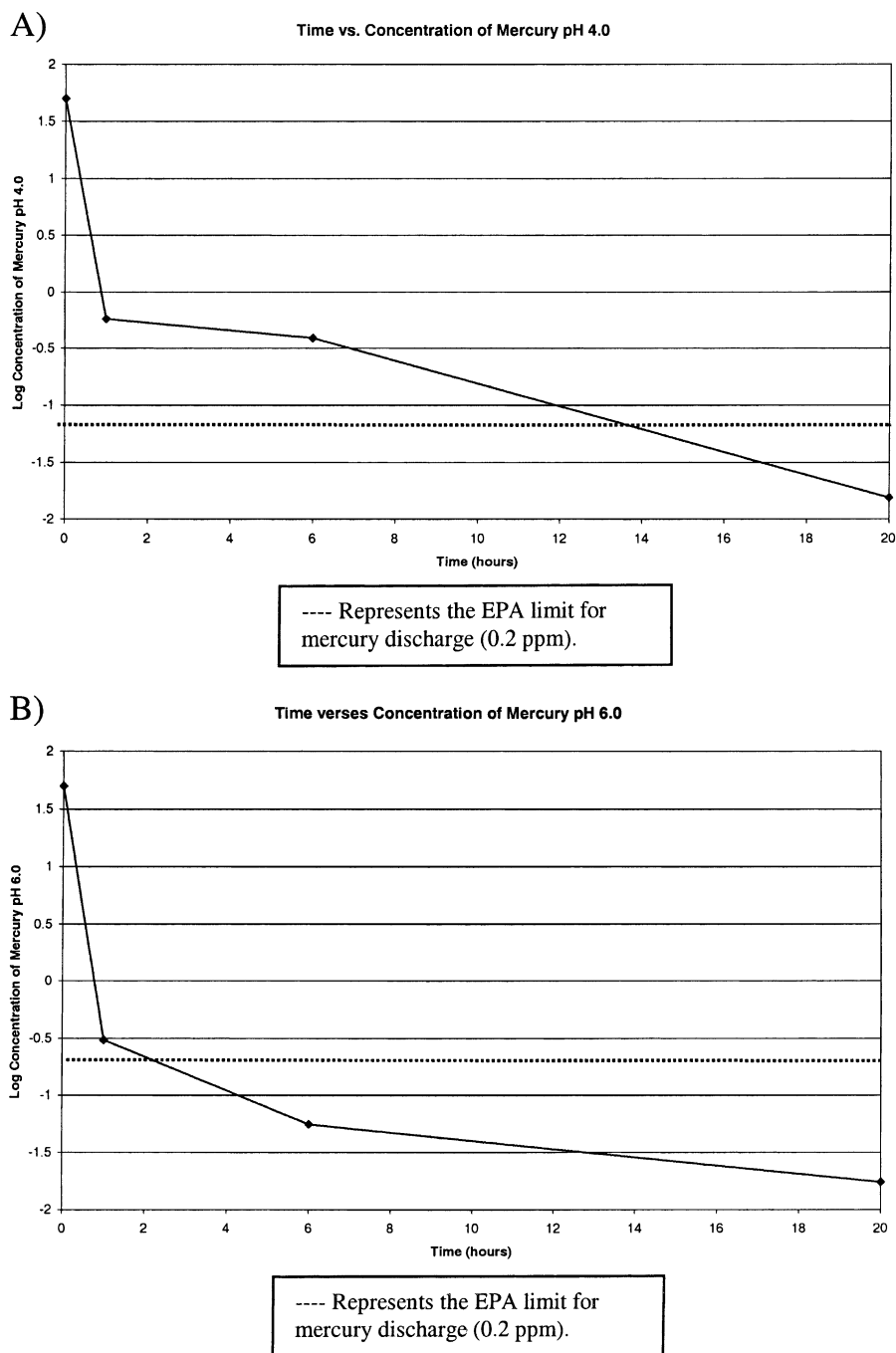


Fig. 5. Removal of mercury at pH 4.0 and 6.0. (A) Removal of mercury at pH 4.0 using a 10% molar dose increase of BDETH<sub>2</sub> ligand; (B) removal of mercury at pH 6.0 using a 10% molar dose increase of BDETH<sub>2</sub> ligand.



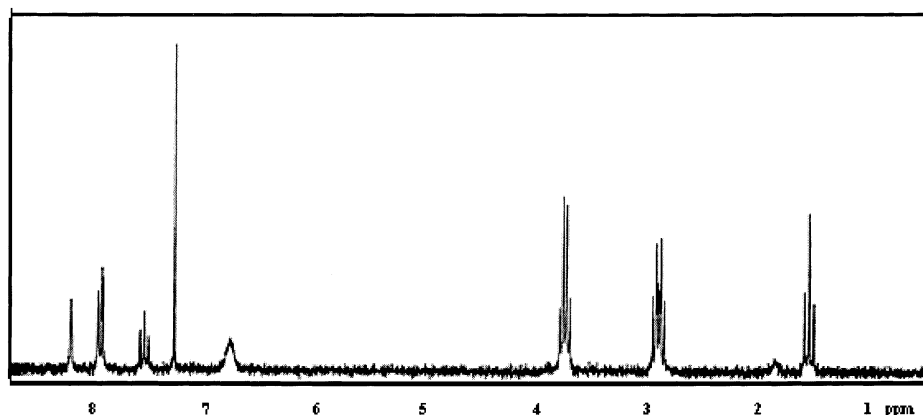


Fig. 6.  $^1\text{H}$  NMR of BDETH<sub>2</sub> ligand.

should be noted that within 1 h of ligand addition, for each experiment, the concentration of lead remaining in solution was below the EPA limit of 5 ppm [5] (Table 1; Fig. 4). For the  $\text{Hg}^{2+}$  reactions, a maximum removal of 99.97% (0.02 ppm) was obtained with the 10% increased dose at 20 h for the pH 4.0 solution (Table 1; Fig. 5). For the  $\text{Hg}^{2+}$  reaction at pH 6.0, a maximum removal of 99.97% (0.02 ppm) was observed at 20 h using a ligand dose increase of 10% (Table 1; Fig. 5).

#### 4. Conclusions

There is a definite need for more stable ligands to meet site remediation, water treatment, and regulatory requirements for heavy metals. Previous studies indicate that many commercial remediation reagents may lack sufficient bonding criteria to produce precipitates that have long-term stability [1,7,8,14]. The BDETH<sub>2</sub> ligand promises to provide the required long-term stability, which will be determined in future leaching studies. The results indicate that a 99.9% removal of lead from a 50.00 ppm aqueous solution may be accomplished using the BDETH<sub>2</sub> ligand at 1:1 mole dose within 6 h at a pH of 4.0. For a 50.00 ppm mercury solution, 99.97% removal occurs within 20 h at a pH of 4.0 and pH 6.0. Reductions to the EPA toxicity limit for lead (5 ppm) were accomplished within 1 h for lead solutions at pH 4.0 and pH 6.0, and the EPA limit for mercury (0.2 ppm) was reached for both solutions, pH 4.0 and pH 6.0, within 6 h [6].

#### Acknowledgements

The ICP facility at the University of Kentucky's Geological Survey in Lexington, Kentucky.

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