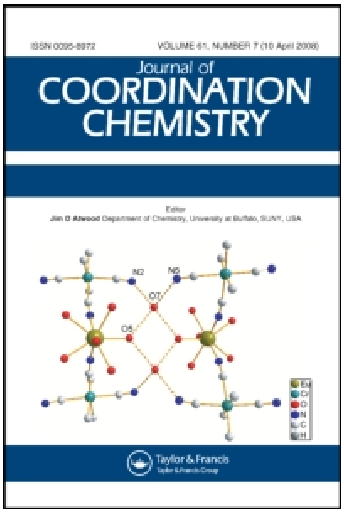

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Preferential adsorption of mercury(II) ions in water: chelation of mercury, cadmium, and lead ions to silica derivatized with *meso*-2,3-dimercaptosuccinic acid

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Preferential adsorption of mercury(II) ions in water: chelation of mercury, cadmium, and lead ions to silica derivatized with *meso*-2,3-dimercaptosuccinic acid

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Meso-dimercaptosuccinic acid (DMSA) covalently attached to silica gel *via* amide bond linkages (DMSA-[silica]) was evaluated as a chelate for Hg(II), Cd(II), and Pb(II). All three metal ions are separately chelated by DMSA-[silica]; 95% of Hg(II) is chelated, 81% of Cd(II), and 74% of Pb(II). When equal molar concentrations of the three metals are allowed to react simultaneously with DMSA-[silica] for 2 h, mercury is preferentially bound (99%) compared to cadmium (13%) or lead (0.4%). Attachment of DMSA to silica surfaces *via* amide bond formation, which increases the thiol to carboxylic acid ratio over free DMSA, is suggested as a factor in enhancing the preference of DMSA-[silica] for mercury.

Keywords: Metal chelation; Mercury(II); DMSA; Silica derivatized chelate

1. Introduction

We are interested in developing strategies for detection of late transition metals in water, in particular, environmentally relevant metals such as mercury, cadmium, and lead. One strategy is based on infrared (IR) spectroscopic detection of surface immobilized chelates. For example, we recently developed a method to detect iron in seawater using an iron-specific chelating biomolecule, desferrioxamine B (DFB), covalently immobilized on a mesoporous silica film [1]. A detection limit of about 50 pM was obtained from the IR spectral signatures of the immobilized DFB upon Fe(III) complexation and the system was used to accurately measure dissolved iron in field tests conducted in subarctic Pacific waters. Extension of this Fe(III) detection method to the detection of late transition metals will require a basic understanding of late transition metal chelation chemistry on immobilized supports. With the extensive number of studies involving metal chelation in solution and the growing interest in immobilized chelates, comparative studies involving chelation reactions in solution *versus* at condensed phases are potentially very useful for illustrating similarities and

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differences in such approaches, and in establishing a basis for their use in detection systems.

A wide variety of small molecules containing "soft" thiol groups (figure 1) coordinate to "soft" elements like Cd, Hg, As, and Pb that prefer covalent bonding to sulfur [2, 3]. Historically, these molecules have been of great interest because of their potential use in medicine. For example, 2,3-dimercaptopropanol-1 (figure 1a), which is also known as British anti-Lewisite (BAL), was discovered and used during the Second World War in reversing the effects of the chemical weapon, Lewisite (2-chloroethenyl–dichloroarsine) [4]. The arsenic from Lewisite bonds to protein–SH groups, inhibiting various enzymatic functions, and it is the competition of BAL for the metal-bound protein that allows it to chelate and remove arsenic from a cell which is ultimately excreted in urine [5]. BAL as well as 2,3-dimercaptosuccinic acid (DMSA, figure 1c) both coordinate a wide variety of heavy metals such as arsenic, mercury, cadmium, and lead and are used medicinally in the treatment of heavy metal poisoning [6]. The activity of compounds such as those listed in figure 1 involves a delicate balance of chemical properties, which are not always easy to predict. For example, while **1a–d** and **1f** are effective as antidotes for acute mercuric chloride poisoning, compound **1e** was found to be ineffective [2].

The work by Fernando [7–10] and others [11–13] demonstrated that many transition metal ions form metal chelates in solution with *meso*-DMSA. In particular, mercury, cadmium, and lead form metal chelates that have been studied using potentiometric titration experiments and IR analysis, as well as comparative studies involving the dimethyl ester of *meso*-DMSA [10]. This study suggests that complexation of Hg(II) to *meso*-DMSA occurs *via* two thiolate groups while for Cd(II) and Pb(II), complexation occurs *via* one thiolate and one carboxylate. Hard–soft acid base theory predicts that Hg(II) will be more thiophilic than either Pb(II) or Cd(II), leading to a preference for the soft thiolate groups in DMSA. However, the formation constants of *meso*-DMSA with Hg(II), Cd(II), and Pb(II) are all large ($>10^{15}$) [7, 14, 15] presumably

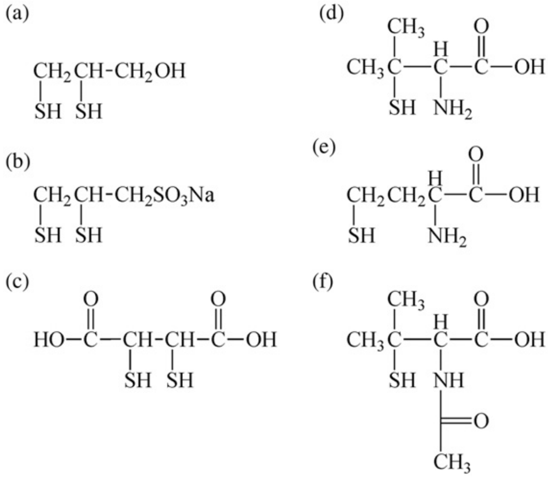


Figure 1. Small thiol containing molecules: (a) 2,3-dimercaptopropanol-1 (BAL), (b) 2,3-dimercaptopropane-1-sulfonate (DMPS, Dimaval), (c) DMSA (succimer), (d) D-penicillamine, (e) homocysteine, (f) *N*-acetyl-DL-penicillamine.

owing to both metal chelation sites, i.e. thiolate and carboxylate. Recently, DMSA immobilized onto magnetic nanoparticles has been used to electrochemically detect Cd, Pb, Cu, and Ag in natural waters as well as for batch metal sorption, including cadmium, mercury, and lead [16, 17]. To further evaluate the chelation of DMSA, we have anchored *meso*-DMSA to a surface *via* one or both of the carboxylic acid moieties attached to silica gel *via* amide bond linkages (DMSA-[silica]). This method of attachment is predicted to increase the thiol to carboxylic acid ratio in comparison to "free" DMSA in solution, which may promote selectivity toward Hg(II). We now report the results of complexation of Hg(II), Cd(II), and Pb(II) to the surface immobilized *meso*-DMSA.

2. Experimental procedures

2.1. *Reagents*

Meso-DMSA, Na_2S (anhydrous), and metal chlorides of Hg(II) (99.999%), Cd(II) (ACS reagent), and Pb(II) ($\geq 98\%$) were purchased from Aldrich and used as received. DMSA was stored in the refrigerator and the metal chlorides stored in a desiccator prior to use. Ethylenediamine (en) was obtained from Aldrich and used as received. The (3-aminopropyl)dimethylethoxysilane (APDMES) was purchased from United Chemical Technologies and Aldrich; *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) was purchased from Aldrich. Fumed silica (Cab–O–Sil HS-5) was obtained from Cabot Corporation.

2.2. *Methods*

IR spectra were collected on a ABB-Bomem FTLA FT-IR equipped with a DTGS detector. All IR spectra were recorded as pressed disks of the sample dispersed in KBr powder. Typically, for each spectrum, 100 scans were co-added at $4\,\mathrm{cm}^{-1}$ resolution. Mercury was measured by using a Tekran 2600 fluorescence spectrometer. The method for analysis of mercury in water is derived from EPA method 1631E and involves oxidation, purge, and trap, and cold vapor atomic fluorescence spectrometry. Cadmium and lead were measured using a PerkinElmer model 3300XL inductively coupled plasma atomic emission spectrometer (ICP-AES). The method of analysis is based on EPA method 200.7 rev. 4.4. An acidified water sample is pumped into the Gemcone nebulizer and into the cyclonic spray chamber, which turns the liquid into a mist. The mist is sent to the plasma where element-specific emission spectra are produced. The spectra are dispersed and the intensities of the emission lines are read by a photosensitive device.

2.3. Meso-*DMSA-Hg(II)*

Aqueous NaOH solutions (0.250 M) were prepared and standardized by titration (three times) using potassium hydrogen phthalate (KHP). Solutions of *meso*-DMSA disodium salt (Na_2DMSA) were prepared *in situ* by adding 2.00 equivalents of NaOH aqueous solution (32.0 mL of 0.250 M NaOH, 8.00 mM) to 1.00 equivalent of DMSA (0.729 g, 4.00 mM) under N_2 using standard Schlenk techniques (as a precautionary measure to prevent oxidation). The sparingly soluble *meso*-DMSA completely dissolves as the sodium salt. A degassed aqueous solution of mercuric chloride (1.086 g, 4.00 mM in 25.0 mL water) was added dropwise *via* cannula to the stirred solution of *meso*-DMSA disodium salt (4.00 mM). A thick white precipitate formed immediately upon mixing. The suspension was stirred for $>$10min, filtered using a fine sintered glass filter, washed three times with 15 mL portions of water, followed by a 15 mL portion of methanol. The washings were combined and analyzed for mercury content (Section 2.4). The air stable precipitate was oven dried at 120°C for $\geq$60 min, after which the solid was resuspended in 30 mL of a 50% water–methanol solution and stirred to remove any trace of unreacted DMSA. The solid was then refiltered and dried at 120° C overnight. The DMSA-Hg(II) product was characterized by potentiometric titration as described in the literature [10].

2.4. Meso-*DMSA-Cd(II) and* meso-*DMSA-Pb(II)*

The preparations of *meso*-DMSA-Cd(II) and *meso*-DMSA-Pb(II) were carried out in a similar manner to that described above for the *meso*-DMSA-Hg(II) complex. Cadmium chloride was used as the source for Cd(II). White, air stable DMSA-Cd(II) compounds formed immediately upon mixing with DMSA solutions. The suspension was allowed to stir for >10 min before workup as noted above. Lead chloride was used as the source of Pb(II). Yellow-green, air stable DMSA-Pb(II) compounds formed immediately upon mixing with DMSA. The suspension was allowed to stir for >10 min before workup as noted above. The DMSA-Cd(II) and DMSA-Pb(II) products were characterized by potentiometric titrations as described [14].

2.5. *Gravimetric determination of free metal ions*

The extent of complexation between *meso*-DMSA and Hg(II), Cd(II), or Pb(II) was evaluated by difference, based on a determination of free metal ions in the filtrate. This was gravimetrically determined by the addition of an excess of Na_2S (which reacts to quantitatively form metal sulfide) to the combined filtrate and washings obtained from the reaction of *meso*-DMSA with metal chlorides (Sections 2.2. and 2.3.). The metal sulfides were then isolated by suction filtration, washed, and dried at 120°C to constant weight. We note that under our experimental conditions, Hg(II) chelation was found to be quantitative only when a slight excess of DMSA ($\geq$2%) was present. When equal molar amounts of DMSA and Hg(II) were used, the amount of mercury chelated was $91.1 \pm 0.2\%$ from an average of three runs. The average amount of Cd(II) and Pb(II) chelated from three runs was $98.1 \pm 0.3\%$ and $99.9 \pm 0.2\%$, respectively. These results are consistent with the observations in the literature [14]. A table of data for the gravimetric experiments is provided as "Supplementary material".

2.6. *Control experiments: gravimetric recovery of free metal ions*

Using the general procedures described above, but in the absence of *meso*-DMSA, a series of six control experiments using 1.00 and 2.00 mM of Hg(II), Cd(II), and Pb(II) chlorides, respectively, were conducted. The addition of an excess of Na_2S resulted in recovery of $99.1 \pm 0.5\%$ of the free metal ions as the metal sulfides.

2.7. *Immobilization of DMSA on silica powder*

The silica powder was calcined in a muffle furnace at 400°C overnight to remove organic contaminants. A Schlenk flask was purged with dry N_2 gas to which 2.00 g of the silica powder was added followed by dropwise addition of 0.50 mL en. Next, a solution containing 1.50 mL of APDMES in 30.0 mL toluene was transferred to the Schlenk flask by cannula under N_2. The suspension was refluxed under N_2 for 3 h followed by the evaporation of the toluene, and drying of the final product (silica-APDMES) in an oven at ~120°C.

The attachment of DMSA to the silica-APDMES (DMSA-[silica]) was carried out by reacting a solution containing *meso*-DMSA in water with an aqueous suspension of the silica-APDMES. The *meso*-DMSA solution was prepared by adding (0.273 g, 0.0015 M) *meso*-DMSA to 25.0 mL warm water under N_2. A 1.00 g sample of the silica-APDMES powder was added to 25.0 mL of water and stirred under N_2 for 30 min, to which 0.280 g EDC was then added. The EDC is used to catalyze amide formation between the amino groups of silica-APDMES and the carboxyl groups of DMSA. The *meso*-DMSA solution was then added to the silica-APDMES/EDC suspension *via* cannula and stirred under N_2 for 5 h. The final product was filtered, washed three times with warm water, followed by three washings with 50% water/ethanol, and then dried in the oven at 120°C.

2.8. *Time-dependent studies of the formation of DMSA-[silica] metal complexes (Hg(II), Cd(II), and Pb(II))*

The same general procedure described above for solution studies was employed except that DMSA-[silica] was used instead of solutions containing *meso*-DMSA, and the incubation times while stirring were increased to 12 h. In each reaction, 0.250 g of DMSA-[silica] (estimated to contain 0.375 mM of attached DMSA [18]) was added to 25.0 mL of distilled water and stirred under N_2 for 30 min. An equivalent amount of the metal chloride (0.375 mM) was added to 25.0 mL of distilled water and stirred under N_2 for 30 min and then this solution was added under N_2 to the DMSA-[silica] suspension. The suspension was stirred for time intervals of 0.5, 2.0, 7.0, and 12 h before workup as described above for the solution studies.

2.9. *Competition studies of formation of DMSA-[silica] metal complexes*

The same general procedure was employed as in the time-dependent studies described above except that the DMSA-[silica] was added to a 25.0 mL solution containing 0.375 mM each of $HgCl_2$, $CdCl_2$, and $PbCl_2$. The mixture was stirred for 30 min, filtered (fine sintered glass), washed, and the filtrate was collected. The resulting solution was analyzed for Hg, Cd, and Pb at the University of Maine, Sawyer Environmental Chemistry Laboratory [19] (see Section 2.2 for details regarding analysis).

2.10. *Ab initio calculations*

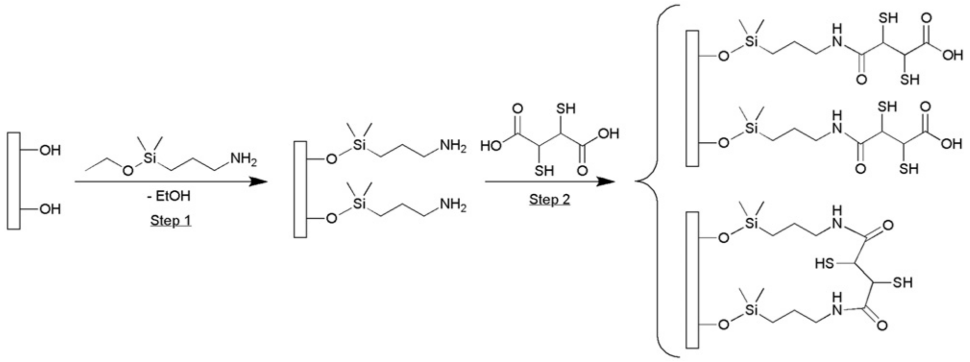
Ab initio IR frequency calculations of model structures of ARH-butylmalonic amide and ARH-ketene zwitterionic structures were performed using Spartan 02 Linux/Unix (Spartan'02, Wavefunction, Inc., Irvine, CA) with density functional and EDF1 model using the 6-31G* as a basis set.

3. Results and discussion

The chelation of aqueous metal chlorides of Cd(II) and Pb(II) with *meso*-DMSA occurs on mixing and is quantitative. With mercury, a slight excess of DMSA to Hg(II) is needed for quantitative recovery, as noted in the literature [14]. In our hands, this excess was $\geq 2\%$ (DMSA to Hg).

The attachment of DMSA to fumed silica is accomplished in two steps. The silica is first modified with APDMES to place primary amino groups at the surface. The *meso*-DMSA is then anchored to the surface *via* formation of amide linkages between the carboxylic acid group(s) of DMSA and surface amino groups, forming DMSA-[silica]. The sequence of chemical steps to attach *meso*-DMSA to a modified silica surface *via* amide bond linkages is illustrated in scheme 1.

IR spectroscopy is utilized at each step to monitor formation of the immobilized DMSA-[silica] material. The spectrum obtained after reaction of DMSA with APDMES-silica is shown in figure 2(a). The attachment of DMSA to APDMES-[silica] *via* amide bond formation is evidenced by appearance of an amide I band at 1638 cm^{-1}. There is a weaker band near 1575–1550 cm^{-1} that we assign to the amide II band; for most amides, the relative intensity of the amide II band is 50% of that of amide I. We attribute the low relative intensity of the amide II band in the case of DMSA-[silica] to the presence of a thiol group on the adjacent carbon atom. In support



Scheme 1. Chemical steps to attach DMSA to silica surface.

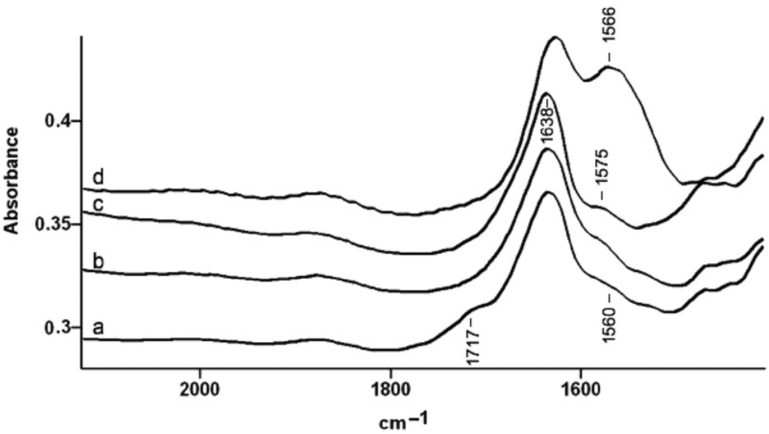


Figure 2. IR spectra. (a) DMSA-APDMES-silica (DMSA-[silica]); DMSA-[silica] reactions with (b) Hg(II), (c) Cd(II), and (d) Pb(II).

of this interpretation, *ab initio* calculations using model compounds of DMSA reacted with various amines were performed. In this case, the simulated IR spectra show the amide II band to be at least a factor of four lower in intensity than the amide I band.

There are two adsorbed species depicted in scheme 1. Specifically, the DMSA can react monofunctionally or difunctionally with the amine groups on the surface. In the former, the attached species is tethered to the surface through one amide linkage and contains a pendant carboxylic acid group whereas in the latter, the surface species is anchored through two amide linkages and therefore possess no carboxylic acid groups. We note that attachment of DMSA does occur monofunctionally to some extent as evidenced by the band at 1717 cm^{-1} in figure 2(a), attributed to a carboxylic acid group of DMSA. While the relative amount of each species depends on the amine density on the silica surface [20], under the reaction conditions used in this work, it is likely that both monofunctionally and difunctionally adsorbed species are present.

The reaction sequence depicted in scheme 1 is an oversimplification of the chemistry occurring on the silica surface. Silica contains approximately equal densities of isolated and hydrogen bonded silanols of which the latter show low reactivity with APDMES. Furthermore, the reaction of APDMES with isolated silanols is not complete [21] and the relative and absolute number of mono- and difunctionally attached DMSA will vary from batch to batch. As a result, all experiments were conducted using the same batch of DMSA-[silica] and the interpretation and conclusions presented are based on relative changes in the degree of chelation of metal ions with the DMSA-[silica].

3.1. *Individual metal chelation by DMSA-[silica]*

The chelation of Hg(II), Pb(II), and Cd(II) by "free" *meso*-DMSA under similar experimental conditions (i.e. rapid stirring) occurs on mixing and is quantitative. In contrast, chelation of these metals by DMSA attached to silica shows a time dependence due to mass transport to the surface of DMSA-[silica] (table 1). Each entry in table 1 represents an independent experiment employing a single metal chloride in contact with the DMSA-[silica]. Each solution was stirred under N_2 for the indicated time, filtered, and washed thoroughly with water and methanol. The combined filtrates were evaluated for the presence of free metal by precipitation as the metal sulfide. The percentage of metal chelated was calculated by taking the difference between the amount of metal chloride added and the amount of metal in the metal sulfide. Control experiments establish that under the experimental conditions employed, quantitative recovery of unchelated metals occurs.

The spectra obtained for "free" *meso*-DMSA and Hg(II), Cd(II) and Pb(II) reacted with "free" *meso*-DMSA are plotted in figure 3. Of particular importance are the two SH stretching modes (2562, 2536 $\mathrm{cm^{-1}}$), the C=O stretching mode of a carboxylic acid (1699 $\mathrm{cm^{-1}}$), and the antisymmetric (1562–1532 $\mathrm{cm^{-1}}$) and symmetric (1393–1373 $\mathrm{cm^{-1}}$) stretching modes of the $\mathrm{COO^-}$ groups. The absence of the SH and $\mathrm{COO^-}$ bands in figure 3(b) suggest complexation of Hg(II) with free *meso*-DMSA *via* two thiolates. This is in contrast to the spectra obtained for the complexation of Cd(II) and Pb(II) (figure 3(c) and 3(d), respectively) in that bands due to SH and $\mathrm{COO^-}$ groups are present. The IR data are consistent with Cd(II) and Pb(II) complexing with one thiolate

Table 1. Time-dependent silica/immobilized DMSA chelation with Hg(II), Cd(II), and Pb(II).

Metal ions added to DMSA-[silica]	30 min (%)	120 min (%)	420 min (%)	720 min (%)	Average value[a] (%)
Hg(II)	73.5	95.3	100.0	100.0	98.4 ± 2.7
Cd(II)	58.5	80.8	83.1	84.3	82.7 ± 1.8
Pb(II)	50.4	73.8	75.1	76.8	75.2 ± 1.5

Times refer to exposure time between metal chlorides and silica/immobilized DMSA before sample workup. The percentages (%) refer to the extent of metal bound to DMSA.

[a] Average values were calculated using data at 120, 420, and 720 min.

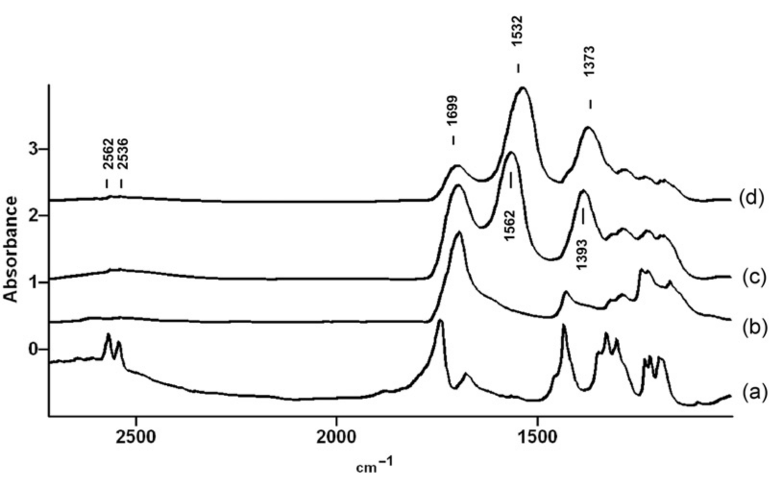


Figure 3. IR spectra obtained for (a) "free" *meso*-DMSA and (b) Hg(II), (c) Cd(II) and (d) Pb(II) reactions with "free" *meso*-DMSA.

and one carboxylic acid site. However, there are differences in the nature of the interaction of Pb(II) and Cd(II) with the carboxylic acid sites. A lower relative intensity of the C=O band at 1699 cm^{-1} of the COO^- antisymmetric band is obtained for Pb(II) compared to the corresponding spectrum obtained for Cd(II). This shows that Pb(II) complexes with a higher percentage of carboxylic acid groups than Cd(II). Furthermore, the COO^- bands in figure 3(d) are shifted to lower frequency compared to figure 3(c), indicating a stronger interaction of Pb(II) with the COO^- groups.

The spectra in figure 2 for the metal ions reacting with DMSA-[silica] are similar in many aspects to their counterparts reacting with free *meso*-DMSA. Specifically, the spectrum obtained after Hg(II) complexation with DMSA-[silica] showed no bands due to COO^- groups whereas a COO^- band was detected in the corresponding spectra for Cd(II) and Pb(II). Moreover, the COO^- band was more intense in the spectrum obtained for Pb(II) and was located at a lower frequency (1566 cm^{-1}) compared to Cd(II) (1575 cm^{-1}), the same trend as for complexation with "free" *meso*-DMSA.

There are two related aspects when comparing the spectra in figures 2 and 3 with the data in table 1 that are noteworthy. The first is that at each time interval, the percentage of metal chelated to DMSA-[silica] is in the order Hg(II) > Cd(II) > Pb(II) (table 1). Attachment of DMSA to the silica *via* amide bond linkages (creating DMSA-[silica]) reduces the number of carboxylic acid sites, which leads to an increase in the ratio of thiol to carboxylic acid. Although the exact structures are unknown, Fernando *et al*. [10] concluded that the complexation of Hg(II) to *meso*-DMSA occurs *via* two thiolate groups, while for Cd(II) and Pb(II), it occurs *via* one thiolate and one carboxylate group. This would make it more difficult for cadmium and lead to achieve the desired thiolate and carboxylate sites for chelation while promoting attachment of mercury at two thiolate sites. This interpretation is fully consistent with the data presented in table 1 and the IR spectra shown in figures 2 and 3.

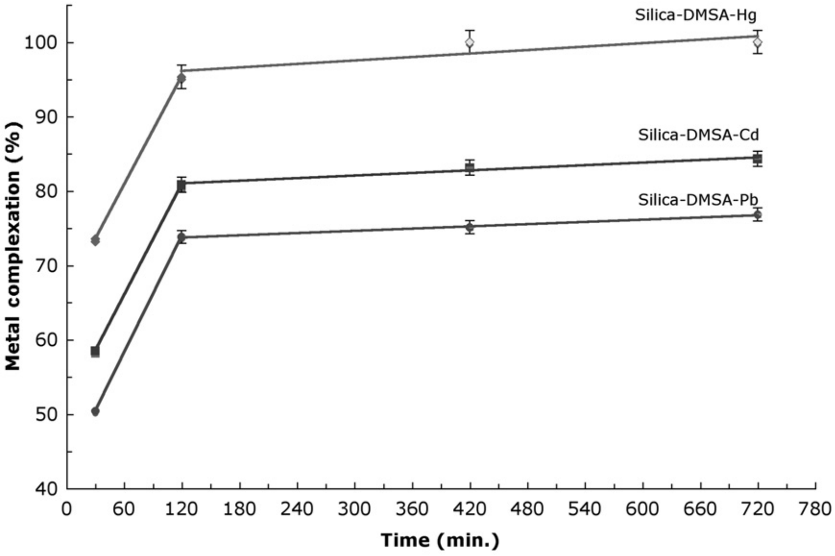


Figure 4. Complexation of Hg(II), Cd(II), and Pb(II) by DMSA-[silica] as a function of time.

Table 2. Chelation of equal amounts of Hg(II), Cd(II), and Pb(II) with DMSA-[silica] after 2 h.

DMSA-[silica] chelation reactions with:	Hg(II) (%)	Cd(II) (%)	Pb(II) (%)
metal-DMSA-[silica] chelates	99.1	13.1	0.4

The second noteworthy aspect of the data, as shown in figure 4, is that the percentage of metal chelated levels out at different percentages for Hg(II), Cd(II), and Pb(II). The average value of the last three data points for each metal (120–720 min) also shows a significant difference in the percentage of metals complexed (see last column in table 1). It is apparent that these levels demonstrate differences in the extent of chelation of the three metals to DMSA-[silica], in contrast to that observed with "free" DMSA, which rapidly and quantitatively chelates all three metals. Clearly, a critical question is, what is the chelation behavior of DMSA-[silica] when the three metals are simultaneously present? An experiment designed to address this question is presented next.

3.2. *Competition studies: simultaneous metal chelation to DMSA-[silica]*

An aqueous solution containing equal molar amounts of Hg(II), Cd(II), and Pb(II) was allowed to mix with DMSA-[silica] for 2 h using the same procedure as employed for individual metal ions. The solution was filtered as before (to remove DMSA-[silica]). However, since precipitation of unreacted metals as metal sulfides would not yield information about the chelation of individual metal ions to DMSA-[silica], the filtrate was collected and analyzed for Hg, Cd, and Pb by ICP-AES. As shown in table 2, the analysis of the data suggests there is a pronounced preference for Hg(II) over Cd(II) and Pb(II). In comparison to the experiments with "free" DMSA, or experiments employing individual metals, there appears to be a clear preference for mercury. We suggest that the characteristics of the solid state DMSA-[silica] material, such as the increased thiol to carboxylic acid ratio, play a critical role in the preference for mercury.

4. Conclusions

The attachment of DMSA to a silica surface dramatically alters the metal-binding characteristics of the chelate by increasing the thiol to carboxylic acid ratio in comparison to "free" DMSA in solution. Covalently attached DMSA to silica gel *via* amide bond linkages (DMSA-[silica]) shows preference toward Hg(II) (95%) compared to Cd(II) (81%) and Pb(II) (74%). More striking, when equal molar concentrations of the three metals are allowed to react simultaneously with DMSA-[silica] for 2 h, Hg(II) preferentially binds (99%) compared to Cd(II) (13%) or Pb(II) (0.4%). The increase in the thiol to carboxylic acid ratio over free DMSA appears to be the major factor in enhancing the preference of DMSA-[silica] for mercury. This approach to engineer specific requirements of metal chelation may be applied toward other chelates to impart selectivity of target metals of interest.

Acknowledgment

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